Mean Amplitudes of Vibration of the *trans*-$IO_2F_4^-$ Anion

Enrique J. Baran

Centro de Química Inorgánica (CEQUINOR/CONICET, UNLP), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, C. Correo 962, 1900-La Plata, Argentina

Reprint requests to Prof. E. J. B.: Fax: (54) 0221 4259485; E-mail: baran@quimica.unlp.edu.ar.

Z. Naturforsch. **59a,** 877 – 878 (2004);
received July 30, 2004

The mean amplitudes of vibration of the *trans*-$IO_2F_4^-$ anion have been calculated from known spectroscopic data between 0 and 1000 K. Bond peculiarities are discussed in comparison with those of *trans*-$IO_2F_5^{2-}$ and of some other structurally related species.

Key words: $IO_2F_4^-$; Mean Amplitudes of Vibration; Bond Properties.

In a recent paper, we have analyzed the mean amplitudes of vibration and bond properties of the novel heptacoordinated *trans*-$IO_2F_5^{2-}$ anion [1]. In order to get a better characterization of the vibrational properties of hypervalent species of this type, we have now performed a similar study of the related *trans*-$IO_2F_4^-$ anion.

Mixtures of the *cis* and *trans* isomers of $CsIO_2F_4$ can be obtained by interaction of $CsIO_4$ with anhydrous HF, BrF_5, ClF_3, ClF_5 or F_2 [2]. The IR and Raman spectra of this salt have been recorded and their assignment supported by a normal-coordinate analysis [2].

The calculations were performed with the method of characteristic vibrations of Müller et al. [3] (cf. also [4, 5]). The necessary vibrational data were taken from [2], and the following geometrical parameters were used: r(I-O) = 1.72 Å, r(I-F) = 1.92 Å, ∠F-I-F = 90°, ∠O-I-F=90° [2].

The obtained results, in the temperature range between 0 and 1000 K, are shown in Table 1.

Table 1. Calculated mean amplitudes of vibration (in Å) of *trans*-$IO_2F_4^-$.

T (K)	$u_{\text{I-O}}$	$u_{\text{I-F}}$	$u_{\text{O...O}}$	$u_{\text{F...F}}$	$u_{\text{O...F}}$
0	0.0372	0.0421	0.051	0.077	0.055
100	0.0372	0.0421	0.051	0.080	0.055
200	0.0373	0.0428	0.051	0.092	0.058
298.16	0.0378	0.0448	0.052	0.106	0.063
300	0.0379	0.0448	0.052	0.106	0.063
400	0.0390	0.0478	0.053	0.119	0.069
500	0.0406	0.0511	0.056	0.132	0.075
600	0.0424	0.0544	0.058	0.143	0.081
700	0.0440	0.0578	0.061	0.154	0.086
800	0.0464	0.0610	0.064	0.164	0.091
900	0.0484	0.0642	0.067	0.174	0.096
1000	0.0504	0.0672	0.070	0.183	0.101

Table 2. Comparison of the mean amplitudes of vibration (in Å and at 298.16 K) of *trans*-$IO_2F_4^-$ with those of structurally related species.

Species	$u_{\text{I-O}}$	$u_{\text{I-F}}$	$u_{\text{F...F}}$	Reference
$IO_2F_4^-$	0.0378	0.0448	0.106	this paper
$IO_2F_5^{2-}$	0.0388	0.0499	0.103	[1]
F_4^-		0.0520	0.139	[8]
IF_4O^-	0.0371	0.0501	0.133	[9]
F_6^+		0.0377	0.081	[10]

From this Table it can be immediately be seen that, as expected, and also in agreement with the respective force constants (f(I-O) = 6.15 and f(I-F) = 3.27 mdyn/Å [2]) the I-O bonds are appreciably stronger than the I-F bonds, the former showing lower mean amplitudes in the whole temperature range. A comparison with the previously investigated *trans*-$IO_2F_5^{2-}$ anion [1], shows the same trends in both cases but the differences between the $u_{\text{I-O}}$ and $u_{\text{I-F}}$-values, at any temperature, are greater in this second case. This situation confirms again the influence of congestion effects in the IF_5 plane, which contribute in an important way to the I-F bond lengthening and weakening [1, 6]. This explains also the weaker I-F bonds in the case of *trans*-$IO_2F_5^{2-}$, when compared with *trans*-$IO_2F_4^-$.

On the other hand, the I-O bonds are somewhat stronger in the present case, probably due to the overall effect introduced by the higher negative charge in *trans*-$IO_2F_5^{2-}$ which causes a general bond weakening [7].

In Table 2 we compare the values of these two species and data of other species closely related to *trans*-$IO_2F_4^-$. A comparison of the presented information shows that the I-O amplitudes of *trans*-$IO_2F_4^-$ and of IOF_4^- are comparable, despite the two different oxidation states of iodine involved in these anions. This demonstrates that even in these anions the iodine-oxygen bonds are essentially double I=O bonds, whereas the formal negative charge is located mainly on the more electronegative fluorine atoms. Besides,

0932–0784 / 04 / 1100–0877 $ 06.00 © 2004 Verlag der Zeitschrift für Naturforschung, Tübingen · http://znaturforsch.com

these results also confirm that in species of this type the axial I-O bonds are scarcely influenced by changes in either the ionic charge or the oxidation state of iodine [7].

Regarding the I-F bonds, there is a clear correlation between its mean amplitude values and the oxidation state of iodine. The octahedral $IF_6{}^+$ cation shows the lowest amplitude, and therefore the strongest bond. In the other two species containing I(VII), the amplitudes are greater, indicating bond weakening with increasing overall negative charge over the anion, i.e. I-F bonds in *trans*-$IO_2F_5{}^{2-}$ are weaker than in *trans*-$IO_2F_4{}^-$. Besides, the I-F bonds in $IF_4{}^-$ are somewhat weaker than in IF_4O^-, in agreement with the lower oxidation state of iodine in the first case.

A further analysis of the data presented in Table 1 shows that the mean amplitude values for the non-bonded atom pairs lie in the order $u_{F...F} > u_{O...F} > u_{O...O}$. This is the same order as that previously found for *trans*-$IO_2F_5{}^{2-}$ [1]. Also, in the present case the non-bonded $F^{\cdots}F$ pair shows the greatest temperature dependence, a fact probably related with the higher ionicity of the I-F bonds [2]. On the other hand, comparing the structurally related species presented in Table 2, it is evident that the $u_{F...F}$ amplitudes shows a similar trend as that found for the related I-F bonds.

Acknowledgement

This work was supported by the Universidad Nacional de La Plata (Project X-339) and the “Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina”, the author being a member of the Research Career from this organization.

[1] E. J. Baran, Z. Naturforsch. **59a**, 527 (2004).
[2] K. O. Christe, R. D. Wilson, and C. J. Schack, Inorg. Chem. **20**, 2104 (1981).
[3] A. Müller, C. J. Peacock, H. Schulze, and U. Heidborn, J. Mol. Struct. **3**, 252 (1969).
[4] A. Müller, E. J. Baran, and K. H. Schmidt, Characteristic Mean Amplitudes of Vibration; in S. J. Cyvin (Ed.), “Molecular Structures and Vibrations”, Elsevier, Amsterdam 1972.
[5] E. J. Baran, An. Asoc. Quím. Argent. **61**, 141 (1973).
[6] K. O. Christe, W. W. Wilson, G. W. Drake, D. A. Dixon. J. A. Boatz, and R. Z. Gnann, J. Amer. Chem. Soc. **120**, 4711 (1998).
[7] J. A. Boatz, K. O. Christe, D. A. Dixon, B. A. Fir, M. Gerken, R. Z. Gnann, H. P. A. Mercier, and G. J. Schrobilgen, Inorg. Chem. **42**, 5282 (2003).
[8] E. J. Baran, J. Mol. Struct. **21**, 461 (1974).
[9] E. J. Baran, Monatsh. Chem. **110**, 715 (1979).
[10] E. J. Baran, Monatsh. Chem. **105**, 1148 (1974).