

PECULIARITIES OF I-F AND I-O BONDS IN DIFFERENT HYPERVALENT SPECIES OF IODINE

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*Dedicated to the memory of the late Prof. Hans J. Schumacher
on the occasion of his 100th birthday*

Abstract

On the basis of calculations of mean amplitudes of vibration a comparative analysis of the properties of I-F and I-O bonds of a wide series of hypervalent iodine compounds is presented. The mean amplitudes of vibration of the I-O bonds are significantly characteristic, whereas those related to the I-F bonds are strongly dependent on the molecular geometry and the oxidation state of iodine, generating important differences between them. The discussion is also extended to some isoelectronic species containing tellurium or xenon.

Resumen

Basado en el cálculo de amplitudes medias de vibración, se presenta un análisis comparativo de las propiedades de los enlaces I-F y I-O en una amplia serie de compuestos hipervalentes de yodo. Las amplitudes medias de vibración para las uniones I-O aparecen claramente características, mientras que las relacionadas a los enlaces I-F dependen fuertemente de la geometría molecular y del estado de oxidación del yodo, generando importantes diferencias entre ellos. La discusión se extiende también a algunas especies isoelectrónicas conteniendo telurio o xenón.

Introduction

As it is known, a rigid polyatomic molecule of a given symmetry can be described in its equilibrium position by a certain number of parameters, e.g. bond distances and interbond angles. However, and as a consequence of the molecular vibrations real molecules are actually not rigid and, thus, their equilibrium parameters cannot be directly observed.

In the analysis of experimental data obtained by modern physico-chemical techniques such as X-ray, electron-diffraction, microwave or high-resolution vibrational (infrared and Raman) spectroscopy, it becomes increasingly important to distinguish between the equilibrium interbond distances and various types of average distances.

The mean amplitudes of vibration are particularly useful in a work of this type and they are usually defined as root-mean square values according to [1]:

$$u_{ij} = \langle (R_{ij} - R_{ij}^e)^2 \rangle^{1/2}$$

which may be regarded as parameters of a non-rigid molecular model. In this equation ij refers to an arbitrary (bonded or non-bonded) atom pair. R_{ij} is the instantaneous interbond distance, and R_{ij}^e the corresponding equilibrium distance and the mean value in the definition involves the statistical-mechanical middle. Consequently, mean amplitudes of vibration are temperature-dependent properties.

On the other hand, under the approximation of small harmonic vibrations, a mean-square amplitude matrix Σ has been devised, and shown to be equivalent to the well-known force-constant matrix, \mathbf{F} . The matrix Σ is temperature-dependent and closely connected to the squared values of u_{ij} , as defined in the equation above [1].

In spectroscopic studies a special importance of the mean amplitudes lies in the fact that they can be used in accurate determinations of molecular force fields, if they can be obtained from electron diffraction-data with sufficient accuracy. In this sense, the mean amplitudes play the same role as Coriolis coupling and centrifugal distortion constants and the frequency data obtained from the vibrational spectra of isotopic species [2] all of which are closely connected to the force field.

Finally, it is interesting to mention that, in a similar way as for vibrational frequencies and force constants, mean amplitudes of vibration can be very characteristic values for both, bonded and non-bonded atoms. This means that if the stretching force constant and the corresponding frequency for a given chemical bond in different molecules are nearly the same, this will also be true for the mean amplitude of vibration of this bond [1,3]. On the other hand, bond strengths, as measured by the force constants are inversely related to the mean amplitude values, i.e., a stronger bond (higher force constant) implies a lower mean amplitude of vibration.

In recent years the vibrational-spectroscopic behavior of an important series of molecules and ions derived from iodine, containing I-F and/or I-O bonds has been investigated. Some compounds of this type are the interesting hypervalent species formally derived from the sp^3d^2 ($IO_2F_4^-$, IOF_4^- , IF_4^- , IOF_5 , IF_5 , IF_6^+) or sp^3d^3 ($IO_2F_5^{2-}$, IOF_5^{2-} , IF_5^{2-} , IOF_6^- , IF_7^-) hybridizations of the central element. In order to attain a wider insight into the vibrational and bond properties of such species we have performed a systematic study of its mean amplitudes of vibration using the available spectroscopic data.

In this communication we summarize and discuss the accumulated information so far, also including results reported by other authors, in order to deduce and emphasize systematic trends related to the I-F and I-O bond peculiarities in these systems.

Calculations

Most of our own calculations were performed with the "Method of the Characteristic Vibrations" developed by A. Müller *et al.* [4] (cf. also [3]), which has provided excellent results for a wide range of molecular systems of different symmetries and bonding characteristics. A detailed discussion of this method has also been published in this Journal, thirty years ago [5].

Results and Discussion

The mean amplitudes of vibration for I-F and/or I-O bonds, calculated at three different temperatures, for all the above mentioned species are shown in Table 1.

Table 1. Mean amplitudes of vibration (in Å) for the I-F and I-O bonds, calculated at three different temperatures.

Species	0 K		298.16 K		500 K		Refer.
	u_{I-O}	u_{I-F}	u_{I-O}	u_{I-F}	u_{I-O}	u_{I-F}	
sp^3d^2							
IF_4^-		0.0467		0.0520			[6]
IF_5		0.0408(E)		0.0430(E)			[7]
		0.0380(A)		0.0394(A)			
IF_6^+		0.0367		0.0377		0.0412	[8]
IOF_4^-	0.0366	0.0456	0.0371	0.0501	0.0395	0.0584	[9]
$IO_2F_4^-$	0.0372	0.0421	0.0378	0.0448	0.0406	0.0511	[10]
IOF_5	0.0358	0.0383(E)	0.0362	0.0397(E)	0.0384	0.0439(E)	[11]
		0.0399(A)		0.0418(A)		0.0469(A)	
sp^3d^3							
IF_5^{2-}		0.0511		0.0607		0.0725	[12]
IF_7		0.0408(E)		0.0430(E)		0.0485(E)	[13]
		0.0378(A)		0.0390(A)		0.0430(A)	
IOF_5^{2-}	0.0373	0.0485	0.0379	0.0551	0.0406	0.0655	[14]
IOF_6^-	0.0369	0.0418(E)	0.0375	0.0444(E)	0.0400	0.0548(E)	[15]
		0.0396(A)		0.0414(A)		0.0465(A)	
$IO_2F_5^{2-}$	0.0380	0.0455	0.0388	0.0499	0.0418	0.0582	[16]

(E): equatorial bonds; (A): axial bonds

The analysis of the presented data allows to remark different interesting aspects:

1. The mean amplitudes of vibration for the I-O bonds are highly characteristic. Observing, for example, the values obtained at 298.16 K they vary only between 0.0362 and 0.0379 Å, and are located in the range that is considered as typical for this bond [3]. On the other hand, these bonds are relatively strong, as suggested by its weak temperature dependence.
2. Although the I-F bond lengths are somewhat longer in the hepta coordinated than in the hexa coordinated species [17], the mean amplitude values of both type of species present similar general trends.
3. The mean amplitudes of vibration of the I-F bonds depend strongly on the ionic charge and the oxidation state of iodine. In both series, these bonds show a certain reinforcement when the oxidation state increases (decrease of the amplitude values) and, at constant oxidation state, a weakening (increase of amplitude values) that parallels the increase of negative charge on the ion. Extreme values are found for IF_6^+ and IF_5^{2-} , in agreement with the fact that in the first species iodine presents the oxidation state +7, a positive charge and the shortest I-F bond (1.75 Å) whereas the other one, with iodine in the oxidation state +3 and two negative charges, presents the longest bond (2.095 Å) [17].

4. Precisely, the anomalously high values found for IF_5^{2-} , which have also been observed in the case of the isoelectronic XeF_5^- anion [18], suggest relatively weak bonds, undoubtedly related to an important congestion effect on the molecular plane, in which the fluorine atoms are practically in contact [18,19].
5. The differences observed for the axial and equatorial I-F bonds in the case of IOF_5 , suggesting that the axial bond is somewhat weaker than the four equatorial ones, confirm the general tendency observed for species of the ZXF_5 type which were exhaustively analyzed some years ago (for a brief review of these results cf. [20]).
6. In general, as it was discussed in detail all through our studies, the most adequate bond model for these hypervalent species is the semi-empirical approach of Rundle and Pimentel [21-23] which, for example, in the case of the hepta coordinated species involves a strongly ionic bond of 6 centers and 10 electrons (6c-10e) for the five equatorial atoms, originated in the interaction of these atoms with a p_x, p_y hybrid orbital of iodine. In this scheme, the axial ligands are covalently bonded to the central atom, using its sp_z hybrid orbital. Therefore, this model, allows a good justification of the relatively weakness of the I-F equatorial bonds in all these species [24].

Finally, it seems also interesting to compare the discussed results with those obtained for isoelectronic species of tellurium and xenon (cf. also [25]). This comparison is shown in Table 2 and, as it can be seen, all these species behave in the expected manner, i.e., the mean amplitudes of vibration of anionic species are usually higher than those of their isoelectronic neutral counterparts. Besides, a higher negative charge on the anion, always generates lower mean amplitude values.

Table 2. Comparison of the mean amplitudes of vibration (in Å and at 298.16 K) of isoelectronic species of iodine, tellurium and xenon.

Species	$u_{\text{x-o}}$	$u_{\text{x-f}}$	References
IF_4^- XeF_4		0.0520 0.0460	[6] [26]
IOF_4^- XeOF_4	0.0371 0.0362	0.0501 0.0446	[9] [7]
IOF_5^- TeOF_5^-	0.0362 0.0375	0.0397(E)0.0418(A) 0.0416(E)0.0447(A)	[11] [27]
IF_5^{2-} XeF_5^-		0.0607 0.0515	[12] [18]
IOF_5^{2-} XeOF_5^-	0.0379 0.0372	0.0551 0.0510	[14] [14]
IOF_6^- TeOF_6^{2-}	0.0375 0.0386	0.0444(E)0.0414(A) 0.0475(E)0.0429(A)	[15] [15]

(E): equatorial bonds; (A): axial bonds

The examples presented in Table 2 also show that the equatorial bonds are generally weaker than the axial ones, in agreement with the predictions of the bonding model mentioned above.

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