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Mean amplitudes of vibration and thermodynamic functions of XeOF_2

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ABSTRACT

The mean amplitudes of vibration of XeOF_2 , a new example of a Xe(IV) compound, were calculated from recently reported spectroscopic and structural data in the temperature range between 0 and 500 K. The results are compared with those of related species and the bond peculiarities of the molecule are also briefly discussed. Its thermodynamic functions were also determined, using the rigid rotator/harmonic oscillator approximation. © 2016 Trade Science Inc. - INDIA

KEYWORDS

XeOF_2 ;
Mean amplitudes of vibration;
Bond properties;
Thermodynamic functions.

INTRODUCTION

Although different older studies suggested the existence of XeOF_2 , only relatively recently pure XeOF_2 could be synthesized and characterized by different spectroscopic methods^[1].

The geometry of XeOF_2 is consistent with a trigonal bipyramidal ZXY_2E_2 , VSEPR arrangement that gives rise to a planar T-shaped geometry (C_{2v} symmetry) in which the two free valence electron lone pairs and the X-O bond occupy the trigonal plane with the two mutually *trans* fluorine atoms perpendicular to that plane.

As part of our studies of vibrational properties of simple inorganic species containing E-O and/or E-F bonds (for a recent review cf.^[2]), and to advance to a better knowledge of the bond characteristics of this interesting molecule, we have now calculated its mean amplitudes of vibration and statis-

tical thermodynamic functions in a wide temperature range.

RESULTS AND DISCUSSION

The calculations of the mean amplitudes of vibration were performed with the method of the "Characteristic Vibrations" of Müller *et al.*^[3] (cf. also^[4,5]). The necessary vibrational-spectroscopic data, obtained from Raman spectroscopic measurements, were taken from the paper of Brock *et al.*^[1]. Only the $\nu_{\text{as}}(\text{XeF}_2)$ stretching mode could not be observed experimentally; their value (573 cm^{-1}) was taken from the theoretical calculations^[1]. The equilibrium geometry of XeOF_2 was also calculated theoretically^[1], and the following geometrical parameters, derived from these calculations, were used: $d(\text{Xe-O}) = 1.809 \text{ \AA}$, $d(\text{Xe-F}) = 1.996 \text{ \AA}$, $\angle \text{OXeF} = 96.4$, $\angle \text{FXeF} = 167.2^\circ$.

TABLE 1 : Calculated mean amplitudes of vibration (in Å) of XeOF₂

T (K)	$u_{\text{Xe-O}}$	$u_{\text{Xe-F}}$	$u_{\text{F}\cdots\text{F}}$	$u_{\text{O}\cdots\text{F}}$
0	0.0397	0.0441	0.063	0.065
100	0.0397	0.0441	0.063	0.066
200	0.0399	0.0452	0.066	0.071
298.16	0.0408	0.0480	0.072	0.079
300	0.0408	0.0480	0.072	0.079
400	0.0425	0.0517	0.078	0.087
500	0.0446	0.0556	0.085	0.095

TABLE 2 : Mean amplitudes of vibration (in Å) for Xe-O and Xe-F bonds in different xenon species, calculated at 298 K

Species	Xe-valence	$u_{\text{Xe-O}}$	$u_{\text{Xe-F}}$	Reference
XeF ₂	Xe(II)	---	0.0474	[6]
XeF ₄	Xe(IV)	---	0.046	[7]
XeOF ₂	Xe(IV)	0.0408	0.0480	this work
XeF ₅ ⁻	Xe(IV)	---	0.0515	[8]
XeO ₃	Xe(VI)	0.039	---	[9]
XeO ₂ F ₂	Xe(VI)	0.0373	0.0468	[10]
XeOF ₄	Xe(VI)	0.0362	0.0446	[11]
XeOF ₅ ⁻	Xe(VI)	0.0372	0.0509	[12]
XeO ₃ F ₂	Xe(VIII)	0.0379	0.0434	[13]
XeO ₄	Xe(VIII)	0.0377	---	[14]

The obtained results, in the temperature range between 0 and 500 K, are shown in TABLE 1. Despite the fact that XeOF₂ is only stable at low temperatures^[1], we have extended the calculations to a wider temperature range, in order to perceive more clearly the general tendencies of its behavior.

In order to attain a first insight into the bond characteristics of XeOF₂, in TABLE 2 we have compared the now obtained results with those of other previously calculated for other xenon compounds.

Remembering that the strength of a given chemical bond could be measured directly by the value of its force constant or of its mean amplitude of vibration, i.e., a strong bond presents a high force constant and a low mean amplitude value, this comparison immediately shows that the Xe-O bond of XeOF₂ presents the weakest so far reported Xe-O bond. On the other hand, also the Xe-F is relatively weak in the present case. It is even weaker than those of the divalent xenon fluoride, XeF₂, and the corresponding Xe(IV) fluoride, XeF₄. However, interestingly, it appears somewhat stronger than the same bond in XeF₅⁻, a behavior which is not totally unexpected

taking into account that this anion presents a pentagonal planar structure in which the two axial lone electron pairs exert a large repulsive force on the Xe-F bonds, forcing the anion to maintain the planarity and contributing to the bond lengthening, the crowding effect in the plane and the polarity of these bonds^[8,15,16].

A similar explanation can be given for the case of XeOF₅⁻, a pentagonal pyramidal species which also presents highly ionic equatorial Xe-F bonds and a concomitant bond weakening^[12,16,17].

In order to have a wider insight into the Xe-O and Xe-F bond strengths we have made a rough estimation of their force constants using the "two-masses" model^[18] and obtained $f_{\text{Xe-O}} = 4.7$ mdyn/Å and $f_{\text{Xe-F}} = 2.6$ mdyn/Å. From these values it is also possible to make an estimation of the bond orders, according to Siebert^[18,19]. For the Xe-O bond a value of 1.4 is determined whereas for the Xe-F bond the value lies slightly below 1.0. These figures indicate a certain degree of double bonding between xenon and oxygen and only single bonds between xenon and the fluorine atoms. These findings are in agree-

TABLE 3 : Statistical thermodynamic functions of XeOF₂ (values in cal/deg.mole)

T (K)	C _p	(H ⁰ - H ₀ ⁰)/T	-(G ⁰ - H ₀ ⁰)/T	S ⁰
0	10.69	8.83	49.63	58.46
100	14.31	10.73	56.34	67.07
200	16.00	11.93	59.87	71.80
298.16	16.43	12.29	60.93	73.22
300	16.46	12.32	61.00	73.32
400	17.66	13.52	64.72	78.23
500	18.35	14.42	67.84	82.26

ment with the relatively high calculated mean amplitude values discussed above, and also with the proposed bonding schema, in which the nearly linear XeF₂ moiety can be described as a 3 center-4 electron bond, generating semi-ionic Xe-F bonds whereas the axial Xe-O bond become relatively stronger as it participate in a normal quasi-localized 2 center-2 electron bond, but also with a certain ionic contribution^[1]. The different strength of both types of bonds becomes also evident by the different temperature dependence of the mean amplitude values.

Regarding the mean amplitudes of vibration of the two non-bonded pairs, as it can be seen from TABLE 1, the values for the F...F pair are always lower than those for the F...O pair, in the full temperature range and differences between them increase with increasing temperature.

Finally, we have calculated the thermodynamic functions, in a wide temperature range, for the ideal gaseous state (unit fugacity), using the rigid rotator, harmonic oscillator approximation^[20,21]. The moments of inertia were calculated with the MOLDRAW program^[22]. The symmetry number is 2.

The results, specific heat (C_p), reduced enthalpy [(H⁰ - H₀⁰)/T], reduced free enthalpy [(G⁰ - H₀⁰)/T] and entropy (S⁰), in the temperature range between 100 and 500 K, are presented in TABLE 3.

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