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Mean Amplitudes Of Vibration Of OsO_3F_2

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ABSTRACT

The mean amplitudes of vibration of OsO_3F_2, one of the rare examples of an EO_3F_2 molecule possessing a trigonal bipyramidal structure, were calculated from known spectroscopic and structural data in the temperature range between 0 and 1000 K. The results are compared with those of related species and the bond peculiarities of the molecule are also briefly discussed.

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KEYWORDS

OsO_3F_2;
Mean amplitudes of vibration;
Bond properties.

INTRODUCTION

The highest oxidation state for any chemical element is +8, and the only elements for which compounds in such a high oxidation state have been characterized are Xe, Ru and Os[1,2]. In the case of osmium, this oxidation state is found in OsO_4, OsO_3N^-, $[OsO_4(OH)_2]^{2-}$, as well as in some neutral and anionic oxofluorides[2,3]. One of this oxofluorides, OsO_3F_2, has been known since 1957 and was prepared by fluorination of OsO_4 with BrF_3[4].

The structure of the crystalline material reveals a polymeric chain structure with distorted octahedral geometry for the OsO_3F_2 units and symmetrical non-linear fluorine bridges[5]. The low vapor pressure of the compound allowed its isolation in an argon matrix in which it remained isolated as a mononuclear molecular species[6,7]. Interestingly, this molecule constitutes an example of the only three known simple inorganic species of EO_3F_2 stoichiometry with trigonal bypiramidal geometry(D_{3h} symmetry) which have been so far prepared and characterized. The other ones are the xenon oxofluoride XeO_3F_2[8], and the recently described $BrO_3F_2^-$ anion[9].

As part of our studies devoted to the investigation of vibrational and bond properties of simple inorganic species containing E-O and/or E-F bonds we have recently calculated the mean amplitudes of vibration of XeO_3F_2[10] and of $BrO_3F_2^-$[11]. As a continuation of these studies we have now performed similar calculations for the related OsO_3F_2 species.

CALCULATIONS

The calculations were performed with the method of the 'Characteristic Vibrations' of Muller et al.[12] (cf. also[13,14]). The necessary vibrational-spectroscopic data were taken from the paper of Beattie et al.[6]. The equilibrium geometry of OsO_3F_2 was theoretically predicted some time ago by using quantum-mechanical ab initio methods at the harthree-fock and MP2 level of theory[15]. The following geometrical parameters, derived from these calculations, were used: d(Os-O)=1.68 Å, d(Os-F)=1.85 Å, <OOsO=120^0, <FOsF=180^0 and <FOsO=90^0(cf. also[9]).

RESULTS AND DISCUSSION

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

As expected, the mean amplitude value for the Os-O bond is comparable to that calculated for OsO_4 (0.0348 Å at 298 K)[16]. Also, the mean amplitude values for the same bond in the OsO_3N^- anion present comparable values(0.0360 Å at 0 K and 0.0366 Å at 298 K)[17].

Besides, and on the basis of the estimated force constant(7.64 mdyn/Å)[9] a bond order of 2.15 can be estimated for the Os-O bond, according to siebert[18,19]. This value points to a relatively strong π contribution to this bond. A comparison with the isostructural species immediately shows that this is the strongest E-O bond of the series(bond orders calculated for the other two species are: 1.37 for $BrO_3F_2^-$ and 1.74 forXeO_3F_2). This higher Os-O bond strength is also clearly reflected in the temperature dependence of the mean amplitude values of this bond, which is the lowest in the series.

TABLE 1: Calculated mean amplitudes of vibration (in Å) of OsO_3F_2

T (K)	$u_{Os\text{-}O}$	$u_{Os\text{-}F}$	$u_{O\ldots O}$	$u_{F\ldots F}$	$u_{O\ldots F}$
0	0.0349	0.0392	0.059	0.053	0.055
100	0.0349	0.0392	0.059	0.053	0.056
200	0.0349	0.0396	0.062	0.054	0.061
298.16	0.0353	0.0411	0.067	0.056	0.066
300	0.0353	0.0411	0.067	0.056	0.066
400	0.0361	0.0435	0.073	0.059	0.073
500	0.0373	0.0462	0.078	0.063	0.079
600	0.0388	0.0490	0.084	0.067	0.086
700	0.0404	0.0519	0.090	0.071	0.092
800	0.0421	0.0547	0.095	0.075	0.097
900	0.0438	0.0574	0.100	0.079	0.103
1000	0.0455	0.0601	0.105	0.083	0.108

Regarding the Os-F bonds, from the estimated force constant of 4.12 mdyn/Å a value of 1.23 can be determined for the bond order. This value shows even a weak π contribution in agreement with which also the Os-F amplitude values present the lowest temperature dependence in the mentioned isostructural series. Unfortunately, they are not data of mean amplitude values for this bond in other osmium compounds. The only so far available data are those of OsF_6(0.0372 Å at 0 K and 0.0384 Å at 298 K)[20] which lie only slightly lower than those calculated here.

The mean amplitude values for the non bonded pairs are in the order $u_{F\cdots F}<u_{O\cdots F}<u_{O\cdots O}$ at room temperature, but with increasing temperatures the values for the O···O-pair become lower than those of the O···F-pair. On the contrary, in the case of XeO_3F_2 the observed ordering is $u_{O\cdots O}<u_{O\cdots F}<u_{F\cdots F}$ in the full temperature range whereas in $BrO_3F_2^-$ it is $u_{O\cdots F}<u_{O\cdots O}<u_{F\cdots F}$, also in the full temperature range.

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