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SHORT COMMUNICATION

Vibrational Properties of the SeO_2F^- Ion

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Recently, we have calculated the vibrational properties of BrO_2F [1] and discussed some aspects of the bond properties of this molecule. In relation with this work and in order to obtain a wider insight in the molecular properties of this type of compounds it seems now interesting to perform a similar analysis of the isoelectronic SeO_2F^- ion.

The infrared and Raman spectra of this later species as the cesium and potassium salts have been recently measured and a complete assignment of its fundamental vibrations has been given [2] .

For the calculation of force constants we have used the "Kopplungsstufenverfahren" proposed by Fadini [3] , the G matrix elements given by Cotton and Horroks [4] in their study of thionyl halides and the frequency data from $KSeO_2F$ [2]. The following geometrical parameters have been estimated, by comparison with related species: d(SeO) = 1.58 Å, d(SeF) = 1.74 Å and both FSeO and OSeO angles = 108°.

The obtained set of principal valence force constants derived from the corresponding symmetrized force constants [4] is given in Table 1. The FSe/SeO, SeO/OSeO, FSe/FSeO,

FSe/OSeO, FSeO/OSeO and SeO/FSeO interaction force constants are negligibily small and in all cases close to zero.

TABLE 1

Valence Force Constants for SeO_2F^-

Constant	mdyn/Å	Description
f_r	6.29	Se-O stretch
f_R	1.56	Se-F stretch
f_b	0.39	OSeO bend
f_a	0.32	FSeO bend
f_{rr}	0.47	SeO/SeO interaction
f_{aa}	0.11	FSeO/FSeO interaction

The mean vibrational amplitudes have been calculated using the "Method of the Characteristic Vibrations" [5-7] . Results at different temperatures are presented in Table 2.

A comparison of the force constants and mean amplitudes of vibration of SeO_2F^- with the corresponding values for BrO_2F, shows the trends expected for such an isoelectronic pair [6] : the force constants of the anion are slightly lower than those of the molecule whereas the corresponding amplitude values show the opposite behavior.

The force constant for the Se-O bond of SeO_2F^- lies higher than in the isoelectronic SeO_3^{2-} ion (4.55 mdyn/Å) [8] and even than in the hexavalent SeO_4^{2-} ion (5.81 mdyn/Å) [8]. On the contrary, the force constant of the Se-F bond appears as extremelly small. A totally similar behavior was observed in BrO_2F [1] and ClO_2F [9] .

Bond orders, calculated with the simple method of Siebert [8] , are 0.63 for the Se-F bond and 1.50 for the Se-O bond. All this results sustain the supposition [2] of a large ionic character for the selenium-fluorine bond.

TABLE 2

Mean Amplitudes of Vibration for SeO_2F^- (in Å)

T (K)	u_{Se-O}	u_{Se-F}	$u_{O..O}$	$u_{F..O}$
0	0.0376	0.0509	0.064	0.071
100	0.0376	0.0510	0.065	0.072
200	0.0377	0.0534	0.069	0.080
298.16	0.0381	0.0580	0.075	0.089
300	0.0381	0.0581	0.075	0.090
400	0.0391	0.0635	0.082	0.100
500	0.0406	0.0690	0.089	0.109
600	0.0423	0.0743	0.096	0.118
700	0.0441	0.0795	0.103	0.127

The high values for the mean amplitudes of vibration of this later bond and its large temperature dependance, which is apparently typical for bonds with strong ionic character [10,11] , also support this supposition. On the other hand, the figure obtained for the Se-F amplitude is one of the highest known values for such a bond. Only for the equatorial Se-F bonds in SeF_5^- a similar high value is found [12] and also in this case important ionic contributions are expected [13] . For other species containing Se-F bonds, mean amplitudes of vibration are usually found to lie around 0.400 Å at room temperature [6,11,14] .

Finally, it is worthy to mention that the Se-O amplitude values are found in the range which is characteristic for this bond [6,14] .

In conclusion, this calculations shows that the SeO_2F^- anion behaves in a similar way as other species of this type such as BrO_2F and ClO_2F. The Se-O bond shows a high degree of double bonding character as reflected by the values of the force constant and the respective bond order. On the other hand, in the case of the Se-F bond the low value of the force constant and the high value of the corresponding mean vibrational amplitudes as well as its large temperature dependance can be attributed to a large ionic character, also pointing to the possibility of some fluoride-bridging between the SeO_2F^- ions in the crystal lattices, as has been suggested earlier [2,15] .

All the calculations were performed using an IBM/360 computer (CESPI, Universidad Nacional de La Plata).

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