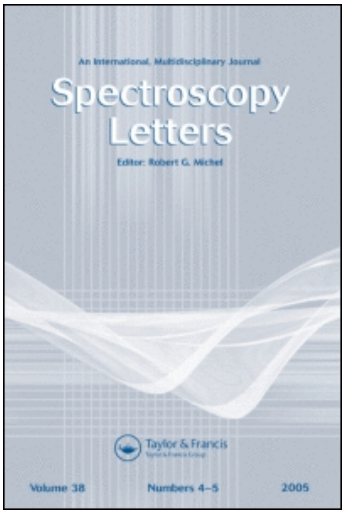

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Vibrational Properties of Bromyl Fluoride

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VIBRATIONAL PROPERTIES OF BROMYL FLUORIDE

Key words: bromyl fluoride, force constants, mean amplitudes of vibration, bond properties.

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Recently the Raman spectra of liquid and solid bromyl fluoride, BrO_2F, have been obtained and interpreted[1]; therefore, and in an attempt to obtain a deeper insight in the bond properties of this molecule, it seems interesting to determine some of its vibrational properties.

The structure of BrO_2F has been assumed to be pyramidal (C_s symmetry)[1], so that the molecule posseses the same geometry as ClO_2F, $ClNF_2$ and the thionyl and selenyl halides.

For the calculation of force constants we have used the "Kopplungsstufenverfahren" proposed by Fadini[2-4], the G-matrix elements given by Cotton and Horrocks[5] in their vibrational study of thionyl halides, and the frequency data from liquid bromyl fluoride[1].

The following geometrical parameters have been estimated, by comparison with related species; d(Br-O) = 1.63 Å, d(Br-F) = 1.76 Å and both FBrO and OBrO angles = 108°.

The obtained set of valence force constants derived from the corresponding symmetrized force constants[5], is given in Table 1.

The value for the f_r constant is only a little smaller than that found for the same bond in BrO_3F (6.88 mdyn/Å)[6] but higher than in the isoelectronic BrO_3^- ion (5.28 mdyn/Å)[7] and even in the heptavalent BrO_4^- ion (5.76

TABLE 1

Valence Force Constants for BrO_2F

Constant	mdyn/Å	Description
f_r	6.76	Br-O stretch
f_R	2.25	Br-F stretch
f_b	0.58	OBrO bend
f_a	0.38	FBrO bend
f_{rr}	0.00	BrO/BrO interaction
f_{Rr}	0.00	BrF/BrO interaction
f_{aa}	0.12	FBrO/FBrO interaction
f_{rb}	0.00	BrO/OBrO interaction
f_{Ra}	0.02	FBr/FBrO interaction
f_{Rb}	0.00	FBr/OBrO interaction
f_{ab}	0.01	FBrO/OBrO interaction
f_{ra}	0.00	BrO/FBrO interaction

mdyn/Å)[8]. The bond order, calculated by the simple method of Siebert[7], is 1.55. All this results point out to a high degree of double bond character for this bond, whereas the relative small force constant calculated for the Br-F bond (f_R) sustains the supposition[1] of a large ionic character of this later bond, which contributes to the observed strenghtening of the Br-O bond, due to the presence of a partial positive charge on the bromine atom.

Using the "Method of the Characteristic Vibrations (cf.[9-11]) we have also calculated the mean amplitudes of vibration for this molecule. Results, at different temperatures, are collected in Table 2. This calculations also confirms the ionic character of the Br-F bond, because the co-

TABLE 2

Mean Amplitudes of Vibration for BrO_2F (in Å)

T (K)	u_{Br-O}	u_{Br-F}	$u_{O..O}$	$u_{F..O}$
0	0.0368	0.0465	0.060	0.068
100	0.0368	0.0466	0.060	0.068
200	0.0369	0.0478	0.062	0.074
298.16	0.0373	0.0508	0.067	0.082
300	0.0373	0.0509	0.067	0.082
400	0.0382	0.0548	0.072	0.091
500	0.0395	0.0590	0.077	0.099
600	0.0410	0.0632	0.083	0.107
700	0.0428	0.0673	0.088	0.115

rresponding amplitude values lies very close to figures obtained for the same bond in other species in which an important ionic contribution is also expected (for example: ClF_4^- (0.0526 Å at 298 K)[12] and BrF_2^- (0.0505 Å at 298 K)[13]). Also the large temperature dependence observed for these amplitude values is apparently typical for bonds with strong ionic character (cf.[14,15]). On the other hand, Br-O amplitude values are found in the range which is characteristic for this bond[6,11].

Finally, it is whorty of notice that also the isostructural ClO_2F shows a fully analogous vibrational behaviour; i.e., high Cl-O and small Cl-F force constants[16] and high values for the mean amplitude of vibration of the later bond, which also shows in this case a great temperature dependence[17].

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

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