MEAN AMPLITUDES OF VIBRATION OF THE $BrO_3F_2^-$ ANION

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Abstract

The mean amplitudes of vibration of the recently characterized $BrO_3F_2^-$ anion, containing Br(VII), were calculated from its 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 new anion are also briefly discussed.

Resumen

Se calcularon las amplitudes medias de vibración del anión $BrO_3F_2^-$, recientemente caracterizado y conteniendo Br (VII), en base a sus datos estructurales y espectroscópicos, en el intervalo de temperaturas entre 0 y 1000 K. Los resultados se comparan con los de especies relacionadas y se discuten brevemente las propiedades de enlace del nuevo anión.

Introduction

It is well known that there is a definite tendency for the nonmetals of the fourth row of the periodic system (As, Se, Br) to be relatively unstable in its higher oxidation states [1,2]. As a consequence, the synthesis of Br(VII) species involves interesting challenges and the number of compounds containing heptavalent bromine remains relatively scarce, including only $HBrO_4$ and some of its salts [3-6], the derived perbromly fluoride, BrO_3F [7] and salts of the BrF_6^+ cation [8]. Recently, the new $BrO_3F_2^-$ anion could be prepared by reaction of BrO_3F with strong fluoride ion donors [9]. The single-crystal X-ray structural analysis of the salts $[NO]_2[BrO_3F_2][F]$ and $[N(CH_3)_4][BrO_3F_2]$ confirm the D_{3h} symmetry of the new anion [9].

The found geometry coincides with the VSEPR prediction [1,10], that states the $BrO_3F_2^-$ anion should present a trigonal bipyramidal structure with the three oxygen atoms occupying the equatorial positions and the two fluorine atoms located on the axial positions. Interestingly, $BrO_3F_2^-$ is so far the only third known EO_3F_2 trigonal bipyramidal species. The other two are XeO_3F_2 [11], and the matrix isolated OsO_3F_2 [12].

Therefore, as a continuation of our studies on vibrational and bond properties of species containing halogen-oxygen and halogen-halogen bonds, it seemed interesting to perform the calculation of the mean amplitudes of vibration of this novel and peculiar anion.

Calculations

Calculations were carried out with the method of the "Characteristic Vibrations" of Müller et al. [13] (cf. also [14]). 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 been published in this Journal, thirty years ago [15]. Briefly, if a given molecular system presents highly characteristic vibrations it is possible to separate this molecule into triatomic "fragments" of the types XY_2 or ZXY and after assignment of vibrational frequencies to these "pseudo molecules" the calculation of the mean amplitude values of these fragments can be made. This means that a vibrational problem of complexity *n* is reduced to the resolution of systems of order $n = 2$ (XY_2 fragments) or $n = 3$ (ZXY fragments). For the present case, the investigated anion was decomposed into the following "fragments": BrO_2, BrF_2 and FBrO.

The employed vibrational-spectroscopic data, taken from the paper of Lehmann and Schrobilgen [9] were: $\nu_s(BrO_3) = 800$; $\nu_s(BrF_2) = 440$; $\nu_{as}(BrF_2) = 500$; $\delta(BrO_3)$out of plane = 460; $\nu_{as}(BrO_3) = 900$; $\delta(BrO_3)$in plane = 395; $\delta(BrF_2) = 228$; $\rho(BrF_2) = 410$ cm^{-1} respectively. The necessary geometrical parameters (d(Br-O) = 1.60 Å; d(Br-F) = 1.86 Å; <OBrO = 119°; <FBrF = 179° and <FBrO = 90°) were derived from the crystallographic data, obtained at -173 °C, for the salt $[NO]_2[BrO_3F_2][F]$ [9]. The energy-minimized gas-phase structure of the $BrO_3F_2^-$ anion, determined by different quantum mechanical approximations, showed comparable values [9].

Results and discussion

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

Table 1. *Calculated mean amplitudes of vibration (in Å) of the* $BrO_3F_2^-$ *anion.*

T (K)	u_{Br-O}	u_{Br-F}	$u_{O...O}$	$u_{F...F}$	$u_{O...F}$
0	0.0385	0.0481	0.059	0.063	0.051
100	0.0385	0.0482	0.059	0.064	0.051
200	0.0386	0.0498	0.061	0.066	0.053
298	0.0392	0.0534	0.065	0.072	0.057
300	0.0392	0.0534	0.065	0.072	0.057
400	0.0404	0.0579	0.069	0.078	0.062
500	0.0421	0.0626	0.074	0.085	0.067
600	0.0440	0.0673	0.080	0.091	0.072
700	0.0460	0.0717	0.085	0.097	0.077
800	0.0481	0.0760	0.089	0.103	0.082
900	0.0502	0.0802	0.094	0.109	0.086
1000	0.0522	0.0842	0.098	0.115	0.091

To attain a clearer insight into the bond peculiarities of $BrO_3F_2^-$ it is worth comparing these values with those calculated for some related bromine species. This comparison is shown in Table 2.

It should be remembered that, in a similar way to 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 [14]. 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.

An analysis of the presented data immediately shows that, independently from the oxidation state of bromine, the geometry and the charge of the different species, the mean amplitude values of the bromine-oxygen bonds are highly characteristic. Notwithstanding, and unexpectedly, this bond presents the highest value mean amplitude in $BrO_3F_2^-$, indicating the weakest Br-O bond. Its strength appears comparable to that of BrO_4^- but it is slightly weaker than that of all the other Br(VII) species even that of the Br(V) species.

On the basis of the calculated force constants [9] a bond order of 1.37 can be estimated for the Br-O bond, according to Siebert [16,17]. This value, which is also comparable to that calculated for BrO_4^- (1.3) [18], points to a relatively weak π contribution to the Br-O bond. This negligible contribution, together with the presence of a negative charge over the anion, may be in great part responsible for the bond weakness, which is also reflected in the relatively important temperature dependence of the mean amplitude values for this bond, for which an increment of about 35% is observed between 0 and 1000 K (cf. Table 1).

Table 2. *Comparison of the mean amplitudes of vibration (in Å and at 298.16 K) of $BrO_3F_2^-$ and some related species*

Species	u_{Br-O}	u_{Br-F}	Reference
BrO_3F	0.037	0.045	[19]
BrF_6^+		0.0405	[20]
$BrO_3F_2^-$	0.0392	0.0534	this work
BrO_4^-	0.039		[18]
$BrOF_3$	0.0359	0.0442 (eq)*	[21]
		0.0478 (ax)*	
$BrOF_2^+$	0.0349	0.0432	[22]
$BrOF_4^-$	0.0373	0.0521	[23]
$BrO_2F_2^-$	0.0380	0.0591	[24]
BrF_2^-		0.0550	[25]

* *(eq): equatorial bonds; (ax): axial bonds.*

The Br-F bonds also present comparatively high mean amplitude values, which are the highest for all the so far known Br(VII) species possessing such a bond. Interestingly, these values are also higher than those calculated for the Br(V) species $BrOF_3$ and $BrOF_4^-$. Besides, this bond also shows an important temperature dependence, with an increment of about 75%

between 0 and 1000 K. For the three tabulated Br(VII) compounds the strength of the Br-F bonds can be clearly correlated with the overall charge on each of these species. The positive BrF_6^+ presents the strongest whereas the negatively charged $BrO_3F_2^-$ species shows the weakest Br-F bond. The neutral BrO_3F molecule presents an intermediate strength.

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References

[1] Huheey, J. E.; Keiter, E. A.; Keiter, R.L. *Inorganic Chemistry. Principles of Structure and Reactivity*, 4th.Edit., Harper-Collins: New York, **1993**.

[2] Baran, E. J. in *Albert Einstein: a Cien Años de sus Trabajos más Importantes y a Ochenta de su Visita a la Argentina* (Weissmann, M.D.; Baran, E.J.; Eds.), Academia Nacional de Ciencias Exactas Físicas y Naturales: Buenos Aires, **2005**, pp.157-179.

[3] Appelman, E. H. *J. Am. Chem. Soc.* **1968**, *90*, 1900.

[4] Appelman, E. H. *Inorg. Chem.* **1969**, *8*, 223.

[5] Appelman, E. H. *Inorg. Synth.* **1971**, *13*, 1.

[6] Baum, K.; Beard, C. D.; Grakauskas, V. *J. Am. Chem. Soc.* **1975**, *97*, 267.

[7] Appelman, E. H. *J. Am. Chem. Soc.* **1969**, *91*, 4561.

[8] Gillespie, R. J.; Schrobilgen, G.J. *Inorg. Chem.* **1974**, *13*, 1230.

[9] Lehmann, J. F.; Schrobilgen, G. J. *J. Am. Chem. Soc.* **2005**, *127*, 9416.

[10] Mingos, D. M. P. *Essential Trends in Inorganic Chemistry*, Oxford University Press: Oxford, **1998**.

[11] Claassen, H. H.; Houston, J. L. *J. Chem. Phys.* **1971**, *55*, 1505.

[12] Hope, E. G.; Levason, W.; Ogden, J. S. *J. Chem. Soc. Dalton Trans.* **1988**, 61.

[13] Müller, A.; Peacock, C. J.; Schulze, H.; Heidborn, U. *J. Mol. Struct.* **1969,** *3*, 252.

[14] Müller, A.; Baran, E. J.; Schmidt, K. H. in: *Molecular Structures and Vibrations* (Cyvin, S.J.; Ed.), Elsevier: Amsterdam, **1972**, pp.376-391.

[15] Baran, E.J. *An. Asoc. Quím. Argent. (This Journal)***,** **1973**, *61*, 141.

[16] Siebert, H. *Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie*, Springer: Berlin, **1966**.

[17] Fadini, A.; Schnepel, F. M. *Schwingungsspektroskopie: Methoden. Anwendungen*, Thieme Verlag: Stuttgart, **1985**.

[18] Baran, E.J.; Aymonino, P. J.; Müller, A. *An. Asoc. Quím. Argent. (This Journal),***1970**, *58*, 7.

[19] Baran, E. J.; Aymonino, P. J. *Z. Naturforsch.* **1972**, *27b*, 1568.

[20] Baran, E. J.; Lavat, A. E. *Indian J. Pure Appl. Phys.* **1982**, *20*, 152.

[21] Baran, E. J. *Z. Naturforsch.* **2002**, *57a*, 205.

[22] Baran, E. J. *Z. Naturforsch.* **2002**, *57a*, 837.

[23] Baran, E. J. *Monatsh. Chem.* **1979**, *110*, 715.

[24] Baran, E. J. *Z. Naturforsch.* **2001**, *56a*, 601.

[25] Baran, E. J. *J. Fluorine Chem.* **1998**, *92*, 119.