Gas-phase Molecular Structures of BrF_5 and IF_5: Information from Electron Diffraction and Rotational Constant Data

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Summary Geometrical data for IF_5 and BrF_5 have been deduced from a combination of electron diffraction measurements and rotational constants measured by microwave spectroscopy.

RECENT microwave studies by Bradley, Brier, and Whittle[1,2] have yielded rotational constants for $^{79}BrF_5$, $^{81}BrF_5$, and IF_5, and have demonstrated that these molecules have C_{4v} symmetry in the gas phase. The spectroscopic data alone are not sufficient to determine the molecular structures, but the rotational constants taken together with electron diffraction results enable the structures to be evaluated with reasonable confidence. Electron diffraction data were collected photographically on the Balzers KDG2 instrument at the University of Manchester Institute of Science and Technology, and processed at Cambridge using published procedures.[3] The electron diffraction data for BrF_5 were obtained in this study. Hewitt, Robiette, and Sheldrick[4] obtained the data for IF_5 which have been further refined since the rotational constant became available.

Three geometrical parameters are necessary to define a C_{4v} model for XF_5 with four equatorial (eq) and one axial (ax) fluorine atoms. These were chosen as $r(XF)_{mean}$, the weighted mean XF bond length; $\Delta(XF)$, the difference between the two types of bond length $[\Delta = r(XF)_{eq} - r(XF)_{ax}]$; and the angle F_{ax}–X–F_{eq}. The parameters refined were those of the average structure,[5] in which distances are described as r_α: r_α distances were interconverted with the observed electron diffraction distances r_a by means of previously calculated perpendicular amplitude corrections.[6] Geometrical parameters obtained from refinements on electron diffraction data alone are listed in the Table, together with rotational constants (designated B_α) calculated from these structures, and for comparison the observed rotational constants B_0 in the vibrational ground states. B_0 is in general almost always greater than B_α.[7] The harmonic force fields for BrF_5 and IF_5 are poorly determined[8] at the present time and therefore the differences $(B_0 - B_\alpha)$ cannot be calculated with any precision. It is likely however, that the values of $(B_0 - B_\alpha)$ lie in the range 0—5 MHz.

For BrF_5 the calculated values of B_α are 4·5 MHz less than the corresponding values of B_0. The calculated isotopic shift [$B(^{79}BrF_5) - B(^{81}BrF_5)$, designated δ in the Table], which should be almost the same for B_α as for B_0,

TABLE

Structural parameters, with estimated standard deviations in parentheses, for BrF_5 *and* IF_5.[a]

	BrF_5		IF_5	
	Gas[b]	Crystal[c]	Gas[b]	Crystal[d]
$r(XF)_{mean}$	1·756 (0·003)		1·861 (0·005)	
$r(XF)_{eq} - r(XF)_{ax}$ ..	0·085 (0·008)		0·025 (0·024)	
$\angle F_{ax}$–X–F_{eq} ..	84·8 (0·1)	84·5 (average)	81·9 (0·1)	80·9 (0·2)
$r(XF)_{eq}$	1·774 (0·003)	1·78 (average)	1·869 (0·005)	1·892 (0·005)
$r(XF)_{ax}$	1·689 (0·008)	1·68	1·844 (0·025	1·862 (0·010)
B_α (calc.)	3094·7 (6·5)[e] 3092·3 (6·5)[f]		2721 (20)	
δ_α (calc.)[g]	2.425 (0·008)		—	
B_0 (obs.)	3099·267 (0·007)[e,h] 3096·831 (0·007)[f,h]		2727·55 (0·05)[i]	
δ_0 (obs.)[g]	2·436 (0·010)		—	

[a] Distances in Å; angles in degrees; rotational constants in MHz. [b] This work. [c] Ref. 9. No errors quoted. [d] Ref. 10. IF_5 molecule in $IF_5 \cdot XeF_2$ molecular crystal. Bond lengths are those corrected for liberation. [e] $^{79}BrF_5$ isotopic species. [f] $^{81}BrF_5$ isotopic species. [g] $\delta = B(^{79}BrF_5) - B(^{81}BrF_5)$. [h] Ref. 1. [i] Ref. 2.

agrees within experimental error with the observed shift in B_0. If $r(\mathrm{BrF})_{\mathrm{mean}}$ and $\Delta(\mathrm{BrF})$ are calculated directly from the two measured B_0 constants, assuming the electron diffraction angle as the third geometrical parameter, the results obtained are $r(\mathrm{BrF})_{\mathrm{mean}} = 1{\cdot}754$ Å, $\Delta(\mathrm{BrF}) = 0{\cdot}079$ Å (this approximates to a mixed r_s/r_0 structure). This agreement is very satisfactory. For IF_5, the most conspicuous feature of the results is that $\Delta(\mathrm{IF})$ is poorly determined from the electron diffraction data alone. Unfortunately B_α is such a sensitive function of $r(\mathrm{IF})_{\mathrm{mean}}$ and $\Delta(\mathrm{IF})$—a fact reflected in the high standard deviation of B_α in the Table—that the observed rotational constant is of little use in fixing $\Delta(\mathrm{IF})$ more accurately. If $r(\mathrm{IF})_{\mathrm{mean}}$ and $\angle \mathrm{F_{ax}{-}I{-}F_{eq}}$ are taken to be 1·861 Å and 81·9°, then $\Delta(\mathrm{IF})$ would have to be 0·046 or 0·029 Å to yield B_α values of 2727·55 MHz or 2722·55 MHz (*i.e.* assuming $B_0 - B_\alpha = 0$ or 5 MHz, respectively). The estimated standard deviation of 0·005 Å in $r(\mathrm{IF})_{\mathrm{mean}}$, however, implies a standard *deviation of* 0·05 Å in these estimates of $\Delta(\mathrm{IF})$. The various gas-phase estimates of $\Delta(\mathrm{IF})$ are therefore consistent though not at all precise; work is in progress to combine the two types of data in the most suitable way. For both molecules agreement with crystallographic determinations is good; these parameters[9,10] are also given in the Table. In particular, $\Delta(\mathrm{IF})$ from the librationally-corrected *X*-ray bond lengths is $0{\cdot}030 \pm 0{\cdot}012$, which lends further confidence to the gas-phase values.

BrF_5 and IF_5 are often used as illustrations of the valence-shell electron pair repulsion theory,[11] in which distortions from idealised octahedral co-ordination with angles of 90° at the central atom are ascribed to the effect of the lone pair of electrons. In this connection it is interesting that while IF_5 has the greater angular distortion ($\angle \mathrm{F_{ax}{-}I{-}F_{eq}}$ 81·9°, $\angle \mathrm{F_{ax}{-}Br{-}F_{eq}}$ 84·8°), the lengthening of the equatorial bonds is apparently substantially greater in BrF_5.

We thank Prof. D. W. J. Cruickshank and Dr. B. Beagley for the use of the electron diffraction apparatus and Mr. R. W. Mather for his technical assistance. We also thank the S.R.C. for a Research Studentship for one of us (R.H.B.).

(*Received, October* 13*th*, 1971; *Com.* 1778.)

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