Nuclear Quadrupole Resonance in Hafnium and Zirconium Tetrabromide

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Summary ^{79}Br and ^{81}Br Quadrupole resonance studies of solid $HfBr_4$ and $ZrBr_4$ support the contention that these compounds are isostructural with $ZrCl_4$, containing both terminal and bridging Br atoms; the bridging Br signals have an anomalous temperature coefficient.

Although in the gas phase $ZrBr_4$ and $HfBr_4$ are, like $ZrCl_4$,[1,2] believed to contain discrete tetrahedral molecules, there is some dispute as to their structure in the solid state.[3] A cubic lattice has been reported[4] for both tetrabromides and proposed for $ZrCl_4$,[5] but a recent *X*-ray structure determination[6] of the latter has shown it to contain zig-zag chains in which $ZrCl_6$ octahedra share two edges in such a way that the two terminal chlorine atoms are in a *cis* rather than *trans* location. Since $HfBr_4$ and $ZrBr_4$ are claimed to be isostructural with $ZrCl_4$,[6] which has monoclinic symmetry, $P2/c$ (C_{2h}^4), with two molecules in the unit cell, the ^{79}Br and ^{81}Br quadrupole resonance spectra of the two bromides should each consist of two signals, one characteristic of terminal Br and the other of bridging Br. We have recently detected such signals in both bromides, in agreement with the monoclinic structure.

Table. ^{79}Br Quadrupole resonance frequencies in $ZrBr_4$ and $HfBr_4$ at various temperatures

	T/K	ν_{ter}/MHz	ν_{br}/MHz
$ZrBr_4$	77	61·92	34·10
	195	61·50	34·75
	273	61·27	35·20
	295	61·23	35·35
$HfBr_4$	T/K	ν_{ter}/MHz	ν_{br}/MHz
	77	66·73	41·20
	195	66·33	41·68
	273	66·06	41·98
	295	65·97	42·05

The Br signals were detected on a Decca super-regenerative oscillator spectrometer and the frequencies were measured at several temperatures, as recorded in the Table. The accuracy of measurement (± 10 kHz) is not higher because the resonances were very broad (*ca.* 50 kHz) and weak. However, all ^{79}Br resonances were checked by recording the corresponding ^{81}Br resonances at a frequency ratio $\nu(79)/\nu(81)$ of 1·197. The samples were obtained from Alfa Inorganics and that of $HfBr_4$ had to be annealed at 300 °C before signals were observed.

In both crystals, the lower frequency is assigned to the bridging bromine atom; the frequency ratio (ν_{ter}/ν_{br}) is then *ca.* 1·8 for $ZrBr_4$ and 1·6 for $HfBr_4$, rather higher than the corresponding value in In_2Br_6 (1·2). This difference could be understood[7] as a consequence of the higher charge on the bridging Br atoms in the Zr and Hf compounds and the different stereochemistry; the co-ordination round the metal atom is octahedral rather than tetrahedral, which leads to a larger MXM angle for the bridging halogen (110·5° in $ZrCl_4$). The noteworthy feature of the bridging Br frequencies, however, is their very considerable positive temperature coefficient, to our knowledge the first that has been reported for a bridging halogen atom. This does not appear to be a consequence of any unusually larger thermal motion, for in $ZrCl_4$ the isotropic temperature factor for the terminal chlorine is larger than that for the bridging chlorine.[6]

We have been unable to confirm a previous report[8] of a single ^{79}Br frequency in $ZrBr_4$ of 60·09 MHz at 77 K, although this disagreement could be due to dimorphism.

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