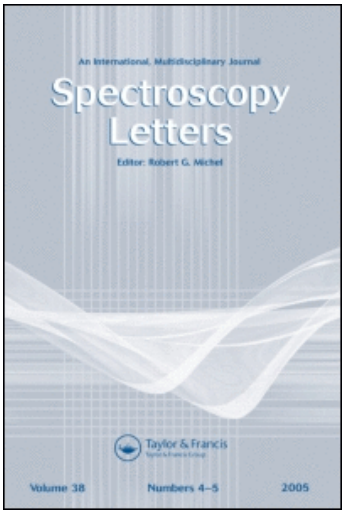

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Fluorine NMR in Zirconium, Hafnium and Thorium Tetrafluorides and f-Orbital Contribution to Interatomic Bonds

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FLUORINE NMR IN ZIRCONIUM, HAFNIUM AND THORIUM TETRAFLUORIDES AND f-ORBITAL CONTRIBUTION TO INTERATOMIC BONDS

KEY WORDS: metal fluorides, NMR spectra, chemical bond.

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Previously[1] we have observed a ^{19}F NMR asymmetric line in polycrystalline ThF_4 in the 6-9 kOe fields, which was ascribed to the anisotropy of the ^{19}F nuclei screening constant. However, the accepted interpretation in the case of a powder sample is not the only possible one, since in the presence of chemically or structurally non-equivalent fluorine atom groups spectrum asymmetry may also arise on account of the difference in the nuclei magnetic screening constants due to non-equivalent positions. This dilemma in the case of polycrystalline samples may be solved only when recording spectra in the highest fields. Non-equivalence of the nuclei may lead to a split of the NMR spectrum into components, corresponding to the various positions. When spectrum asymmetry is due to the anisotropy of the screening constant, field strength rise may but lead to an increase of the total spectrum width, its shape remaining unaltered.

In this connection, ^{19}F NMR spectra in polycrystalline ThF_4, ZrF_4 and HfF_4 were once again investigated in the

23.5 kOe field with the aid of a JNM-4H-100 spectrometer. Some of the obtained spectra are shown in the figure. It is apparent that in our case the application of a higher field leads to a split of the ThF_4 and ZrF_4 fluorine NMR spectra into two separate components. (Note that for ZrF_4[1] in fields up to 9 kOe practically symmetric NMR spectra were recorded.) The table cites the chemical shifts $\langle \delta \rangle$ of ^{19}F NMR spectra gravity centers in Th, Zr, and Hf tetrafluorides, measured[2] in respect to C_6F_6 and recalculated in relation to F_2, as well as spectra doublet splittings. It was also found that doublet splits are directly proportional to the applied

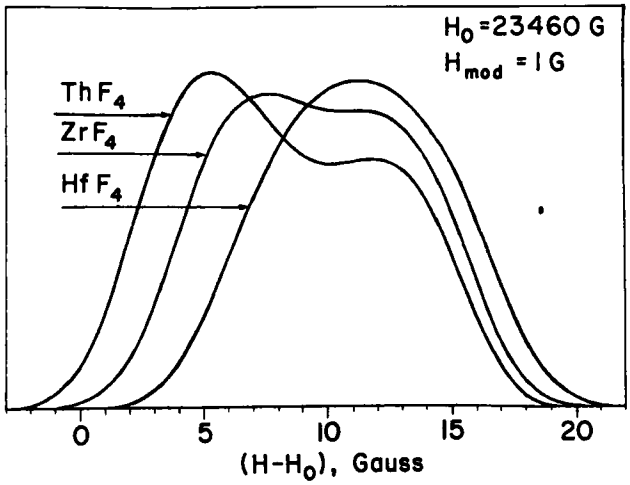

FIG.

Positions and shapes of ThF_4, ZrF_4 and HfF_4 ^{19}F NMR spectra. Zero mark in the $(H - H_o)$ scale corresponds to the ^{19}F NMR signal in gaseous F_2.

magnetic field. This allows for a simple interpretation of the spectrum split into two components as a result of the difference in the screening constants of the two fluorine atom groups in the structure, namely F(A) and F(B), responsible

for the appearance of the lines situated in the high and low fields respectively. The spectra second moments S_2, extrapolated to the zero external field, and the lattice parameters for the compounds discussed are also cited in the table.

TABLE

Chemical Shifts and Doublet Splits in ^{19}F NMR Spectra of ZrF_4 Structure-Type Tetrafluorides.

Fluoride	Lattice Parameters				S_2, Oe^2	$\langle\delta\rangle$	$(\delta_A-\delta_B)$
	a, Å	b, Å	c, Å	β	($H_0 \to 0$)	x10^6	x10^6
ZrF_4	11.71	9.89	7.66	126°09'	10.0±0.4	402±20	150±20
CeF_4*	12.6	10.6	8.3	126°	8.8±0.4	-	150±20
HfF_4	11.70	9.86	7.64	126°05'	-	464±20	0
ThF_4	13.1	11.0	8.6	126°	5.8±0.3	332±20	250±20

*data[3]

Judging by the ratio of the doublet components, 2:1 for ThF_4, it may be inferred that in B loci of structure ThF_4 there are two times more fluorine atoms than in positions A. For ZrF_4 the ratio is ostensibly the same, although, due to a smaller split and broader components as a result of a smaller elementary cell size and correspondingly larger S_2, the difference in the intensities of the NMR line components is less pronounced.

The results seem unexpected in two respects. Firstly, the great difference in the spectra shapes for structurally very close ZrF_4 and HfF_4 is surprising. Secondly, if one proceeds from the already known structural data,[4-6] the resolution of ZrF_4, CeF_4 and ThF_4 fluorine NMR spectra into two

separate lines is unexpected, too. Indeed, the elementary cell of the ZrF_4 structure type, to which all the investigated substances belong, possesses seven structurally non-equivalent fluorine atoms.[4,5] The differences among them, however, are not so great as to possibly cause a spectrum split into two components. An approximate calculation of F-Me and F-F overlap integrals corroborates this conclusion; hence, at first sight, only the HfF_4 spectrum, for which no split whatsoever was revealed, seems usual, whereas the behavior of ZrF_4, CeF_4 and ThF_4 in regard to their NMR spectra appears unusual.

At present there are hardly any grounds to expect any substantially more precise definition of the structural data[4,5] for ZrF_4-type crystals. Especially unlikely is the appearance of marked structural differences between ZrF_4 and HfF_4 because of practically identical Zr^{4+} and Hf^{4+} ionic radii. Hence, it may be concluded that the observed peculiarities in the tetrafluoride group ^{19}F NMR spectra are caused, primarily, by the differences in their electron structure. In particular, both effects are explicable, if one assumes that metal ion f-shells take part in the formation of relatively weak donor-acceptor F-Me bonds for two-thirds of the total number of fluorine ions in ThF_4, ZrF_4 and CeF_4. In HfF_4 such bonds cannot be formed, inasmuch as the Hf^{4+} ion 4f-shell is filled and its electron configuration is f^{14}. This assumption explains, likewise, the relatively great ($\delta_A - \delta_B$) for ThF_4 compared to ZrF_4 and CeF_4, since the actinides 5f-shell is less

screened and, consequently, is capable of giving stronger bonds than the 4f-shell of the rare earth elements.

Now, it is interesting to elucidate which of the 48 fluorine atoms, situated in the Th, Zr and Ce tetrafluoride elementary cells, belong to F(B) atoms, i.e. are bonded with Me ions by f-orbitals (this leading to a shift in their NMR signals towards the low field), and which to the F(A) type, i.e. are not bonded by involving f-orbitals (and possess a "non-shifted" NMR signal). Each of the fluorine atoms is coordinated by two Me^{4+} ions, there being but two structurally non-equivalent types of the said ions, namely Me (1) on the two-fold axes and Me(2) in the general positions. One third of the fluorine atoms - F(1), F(2) and F(5), supposedly belonging to F(A), are bonded only to Me(2) ions, whereas the remaining two-thirds of fluorine atoms - F(3), F(4), F(6) and F(7), ascribed to F(B), are bonded simultaneously with Me(1) and Me(2) ions. Thus, the bonds between these atoms and Me(1) may be assumed to be the reason for the shift of the F(B) atom NMR signal towards the low field.

The essential difference of Me(1)-F and Me(2)-F bonds may be due to the distinction in symmetry of the coordination polyhedra comprising eight fluorine atoms surrounding Me(1) and Me(2) ions. These polyhedra are slightly distorted square antiprisms, those connected with Me(1) possessing the above-mentioned second order symmetry axis. A higher symmetry apparently acts favorably on the formation of Me(1)-F molecular orbitals involving f-shells, whereas with Me(2)-8F polyhedra of low symmetry there is no such possibility.

Data concerning UF_4 magnetic susceptibility anomaly in low temperatures[7] serves as an independent corroboration of the inference regarding the physical difference of fluorine bonds with Me(1) and Me(2) in tetrafluoride structures. To explain some of the features pertaining to this anomaly, it was assumed[7] that the behavior of U(1) and U(2) ions in UF_4 (belonging to the ZrF_4 structure type) is essentially different, mainly in respect to the ion energy spectrum structure in two positions. It is assumed that in this case the main role belongs to the symmetry of the local positions of the U(1) and U(2) ions.

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