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NQR Spectra of ^{93}Nb, ^{181}Ta, ^{35}Cl and ^{79}Br in Niobium and Tantalum Pentahalides

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NQR spectra of ^{35}Cl, ^{79}Br, ^{93}Nb and ^{181}Ta in the series of niobium and tantalum pentahalides have been studied. There has been made a correlation between the carefully studied spectra and X-ray data. It has been shown that NQR spectra of $TaBr_5$, $TaCl_5$ and NbF_5 entirely correspond to their crystal structures. The nature of the chemical bond in the dimeric molecules of M_2Hal_{10} has been discussed.

Introduction

Presently a number of papers dedicated to NQR studies of Nb and Ta pentahalides has been published[1–6]. However, most of the recorded spectra are not complete and usually do not correspond to the known crystal structures of compounds in question. The present work sets out to make the most careful measurements of NQR frequencies of halogen and metal atoms in several niobium and tantalum pentahalides to elucidate correlations between the recorded spectra and the crystal structures of these substances.

Experimental

All measurements were made on the pulse NQR spectrometer IS-Sh-1. For low frequency measurements the pulse coherent panorama NQR spectrometer–relaxomcter PS-1 (SKB IRE Akad. Nauk, S.S.S.R.) was used.

NQR spectra were recorded at 77° K and room temperature (the volume of samples was 2–3 cm^3). Niobium and tantalum pentahalides were carefully purified by rectification[7] followed by a controlled crystallisation carried out in the probe ampules.

Results and Discussion

NQR spectrum of niobium pentachloride (the resonant atoms ^{93}Nb) corresponding to two upper transitions was recorded earlier at 77°K[8]; for all possible transitions the spectrum was studied at room temperature[8]. In NbF_5 we observed an octet (see Table I, Figure 3) where each transition was represented by a doublet of equally intensive lines. Such a spectrum strictly corresponds to the known structure[8] built up by tetramers $(NbF_5)_4$ occupying the sites with the lattice symmetry 2/m (see Figure 1). The symmetry axis 2 passes through the atoms Nb(1) and Nb(1′) and the symmetry plane m through the atoms Nb(2) and Nb(2′) so that only two sorts of atoms – Nb(1) and Nb(2) – are crystallographically non-equivalent and possess equal multi-

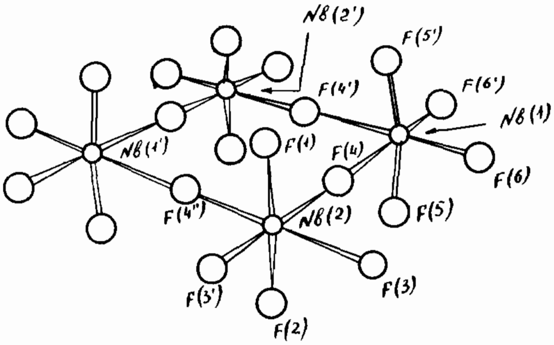

Figure 1. Tetrameric structure of $(NbF_5)_4$.

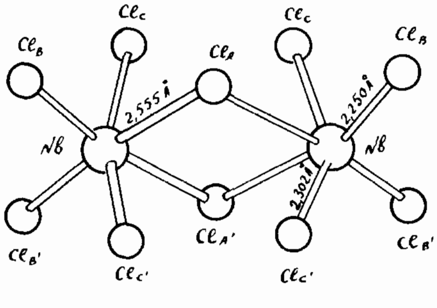

Figure 2. Dimeric structure of $(NbCl_5)_2$.

TABLE I. NQR Frequencies of ^{93}Nb and ^{181}Ta in Niobium and Tantalum Pentahalides.

Compound	Resonant Atom	T° K	Transition Frequencies (MHz)				e^2Qq (MHz)	η %	Relative Intensity
			1/2–3/2	3/2–5/2	5/2–7/2	7/2–9/2			
NbF_5	^{93}Nb	77	5.648 6.116	9.564 9.204	14.610 14.231	19.519 19.050	117.29 114.63	13.7 19.0	I I
		300	5.70 5.70	9.227 9.458	14.208 14.429	19.002 19.270	114.08 116.02	15.9 14.5	I I
TaF_5	^{181}Ta	77	208.44	...	...	–	...	...	
		300	204.136	...	...	–	...	...	
$NbCl_5$	^{93}Nb	77	5.7154	6.052	9.547	12.913	78.28	34.9	
		300	5.4228	6.0621	9.5612	12.9032	78.48	29.8	
$TaCl_5$	^{181}Ta	77	185.53 190.40	241.796 239.776	(378.86)[a] (376.65)	– –	1796.45 1789.54	39.3 41.6	I 2
		300	178.190 183.445	243.676 241.382	(380.29) (377.90)	– –	1798.61 1790.84	36.1 38.6	I 2
$NbBr_5$	^{93}Nb	77	5.272 5.240	4.586 4.616	7.084 7.150	9.706 9.785	59.31 59.75	46.9 46.0	I 2
		300	5.076 5.017	4.616 4.648	7.196 7.266	9.822 9.904	59.87 60.32	43.8 42.6	I 2
$TaBr_5$	^{181}Ta	77	163.101 167.286	181.461 179.760	286.932 284.085	– –	1375.13 1367.09	50.3 52.7	I 2
		300	156.692 161.223	191.900 189.753	(302.01) (299.33)	– –	1437.41 1428.53	43.5 46.3	I 2

[a] Calculated frequencies are given in brackets.

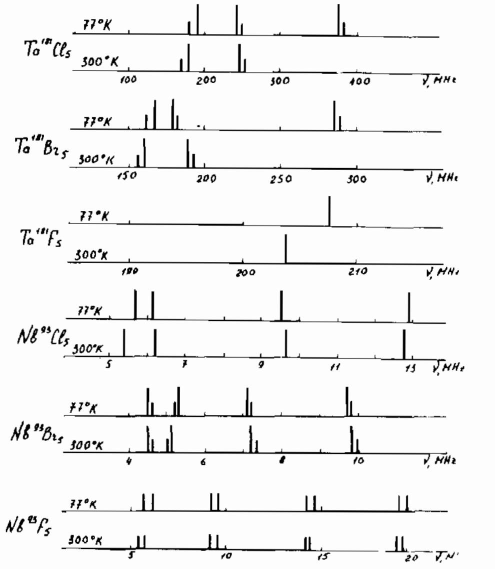

Figure 3. Schematic drawing of NQR spectra of ^{181}Ta and ^{93}Nb in tantalum and niobium pentahalides.

plicity. NQR spectrum of ^{181}Ta in tantalum pentafluoride consists of one line, though as follows from the isomorphism of both crystals[9] it should be a doublet. It is however possible that the spectrum is a close doublet unresolved owing to the large linewidth. In the crystal structure of $NbCl_5$ (the same structure have $NbBr_5$ and $TaCl_5$) the dimeric molecules M_2Hal_{10}[10] occupy two crystallographically nonequivalent positions with the symmetry 2/m (A-type) and with the symmetry m (B-type). In the dimers of A-type the symmetry axis 2 passes through the M atoms, while plane m perpendicular to it through the bridged halogen atoms. Thus only two nonbridged Hal atoms out of eight – Hal_B and Hal_C – are nonequivalent crystallographically. Of two bridged halogen atoms – Hal_A and $Hal_{A'}$ – related by the symmetry axis 2 only one is crystallographically nonequivalent. In dimers B occupying the sites with the lattice symmetry m four nonbridged atoms, Hal_B, $Hal_{B'}$, Hal_C and $Hal_{C'}$, and two bridged atoms, Hal_A and $Hal_{A'}$, are crystallographically nonequivalent. Then bearing in mind that the relative multiplicities of A and B dimers are 1 : 2 we get the number and the intensity ratio of halogen lines in the multiplet: $4\mathrm{Hal_B} : 4\mathrm{Hal_C} : 2\mathrm{Hal_A} : 2(2\mathrm{Hal_B} : 2\mathrm{Hal_C} : 2\mathrm{Hal_{B'}} : 2\mathrm{Hal_{C'}} : \mathrm{Hal_A} : \mathrm{Hal_{A'}}) = \underbrace{2:2:1}_{\mathrm{A}}:\underbrace{2:2:2:2:1:1}_{\mathrm{B}}$

where relative intensity 1 corresponds to the bridged and relative intensity 2 to nonbridged halogen atoms. There is only one crystallographically nonequivalent metal atom for each type of dimers, since in dimer A as well as in dimer B both metal atoms are related by the symmetry plane passing through the bridged halogen atoms. However, because of the double multiplicity of B-dimers the intensity ratio of resonant metal lines in the multiplet is 1 : 2 for each transition.

NQR spectrum of ^{35}Cl in NbCl$_5$, observed experimentally, consists of four low frequency and of two high frequency lines, two of four low frequency lines having double intensities. NQR spectrum of ^{93}Nb is a singlet, *i.e.* it corresponds to one crystallographically nonequivalent Nb atom. The contradiction between the known crystal structure of NbCl$_5$ and the recorded spectrum can only be explained by the difference in crystal phases, *i.e.* by the fact that the modification studied by X-ray method differed from that observed in our experiment. NQR spectrum of ^{35}Cl in TaCl$_5$ (Table II, Figure 4) that was found to be isostructural with niobium pentachloride[10] corresponds to theoretical one for the structure of this type. It consists of six low frequency lines and of three high frequency lines of half intensity. NQR spectrum of ^{181}Ta corresponds to two nonequivalent position of tantalum atom with the population ratio 1:2. Since NQR spectra of ^{79}Br and ^{181}Ta in tantalum pentabromide are exactly analogous with NQR spectra of ^{35}Cl and ^{181}Ta in TaCl$_5$ and correspond to those expected for the known structure of NbCl$_5$[10] one may assume both tantalum pentahalides to be isostructural. NQR spectra of NbBr$_5$ (Table I, Figure 3) may be explained under assumption of the coexistence of two crystallographic modifications

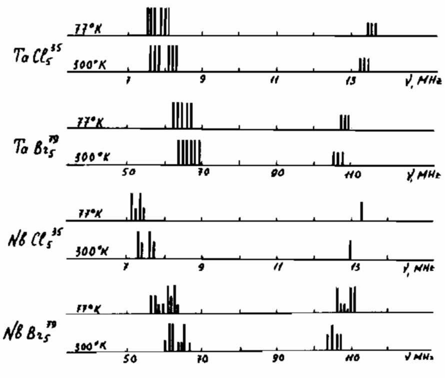

Figure 4. Schematic drawing of NQR spectra of ^{35}Cl and ^{79}Br in tantalum and niobium pentahalides.

TABLE II. NQR Spectra of ^{35}Cl and ^{79}Br in Niobium and Tantalum Pentahalides.

Compound	Resonant Atom	T°K	Line Number								
			"Non-bridged" Atoms						"Bridged" Atoms		
			1	2	3	4	5	6	7	8	9
TaCl$_5$	^{35}Cl	77 ν, MHz	7.535	7.562	7.589	7.941	8.017	8.043	13.535	13.551	13.571
		300 ν, MHz	7.598	7.641	7.663	8.141	8.231	8.261	13.334	13.356	13.377
		$\frac{1}{\nu}\frac{\partial\nu}{\partial T}\times 10^3$ degr^{-1}	−0.0375	−0.0468	−0.0437	−0.1130	−0.1197	−0.1215	0.0666	0.0645	0.0641
TaBr$_5$	^{79}Br	77 ν, MHz	64.973	65.124	65.220	65.220	65.859	66.193	109.292	109.446	109.615
		300 ν, MHz	65.864	66.023	66.167	67.260	67.862	68.190	107.894	108.117	108.250
		$\frac{1}{\nu}\frac{\partial\nu}{\partial T}\times 10^3$ degr^{-1}	−0.0615	−0.0619	−0.651	−0.1403	−0.1364	−0.1354	0.0574	0.0544	0.0588
NbCl$_5$	^{35}Cl	77 ν, MHz	7.218	7.316	7.350	7.444			13.291		
		300 ν, MHz	7.219	7.365	7.612	7.721			13.058		
		$\frac{1}{\nu}\frac{\partial\nu}{\partial T}\times 10^3$ degr^{-1}	−0.0379	−0.030	−0.1599	−0.1662			0.0786		

TABLE III. NQR Frequencies of ^{79}Br in Niobium Pentabromide.

(MHz), 77° K	Relative Intensities	(MHz), 300° K	Relative intensities
"Non-bridged" Atoms			
59.032	I	60.441	I
59.176	3	60.555	2
59.337	2	60.670	2
59.753	I	61.970	I
59.843	2	62.303	I
60.326	I	62.436	2
		62.833	I
"Bridged" Atoms			
106.984	I	105.300	I
107.230	I	105.752	2
107.327	I	106.156	I
107.705	I	106.624	I
108.010	I		

one of which is isotructural with the modification of $NbCl_5$ studied in this work, and the other with that described in the literature[10]. In this case NQR spectrum of ^{79}Br should consist of four high frequency lines and of ten low frequency lines. Actually, NQR spectrum of ^{79}Br in niobium pentabromide at room temperature roughly corresponds (if one considers integral intensities) to such assumption. Attention must be given to the additive splittings of one of the high frequency lines of ^{79}Br in $NbBr_5$ at 77°K. The additive splittings also arise in the low frequency part of the spectrum. It is possible to assume that in the spectrum of $Nb^{35}Cl_5$ the splittings of this kind were not detected because of their negligible magnitude or owing to the large line-widths.

NQR spectrum of ^{93}Nb in niobium pentabromide, as well as that of ^{181}Ta in tantalum pentachloride and pentabromide corresponds to two nonequivalent niobium positions with the population ratio 1:2. Additionally, a rather broad and apparently single line is observed.

As can be seen from Table II (and Figure 4) low frequency triplets in NQR spectra of $MHal_5$ possess an abnormal temperature dependence which has been pointed out previously in one of our papers[4]. The temperature coefficient of the low frequency triplet is 2–2.5 times smaller than that one of the middle frequency, while the temperature dependence of the high frequency triplet is normal. An abnormal temperature dependence of NQR frequencies commonly observed for the halogen atoms bonded to a transition element is explained by the specific character of dative pπ-orbital interactions of halogen atoms. The separation of the low frequency multiplet into triplets with greatly different temperature coefficients corresponds to two types of nonbridged halogen atoms.

Actually, a dimeric molecule consists of two octahedra sharing a common edge (bridged halogen atoms, see Figure 2), Hal_C and $Hal_{C'}$ lying in the equatorial plane while Hal_B and $Hal_{B'}$ (axial atoms) are in the plane perpendicular to that mentioned above. The difference in the electron distribution for the atoms of both types also affects corresponding bond lengths (see Figure 2).

In tantalum pentachloride there is observed an unusual phenomenon of a gradual stabilization of NQR frequencies for ^{181}Ta after putting the sample into liquid nitrogen. For the transitions 3/2–1/2 the frequency is increased and for the transition 5/2–3/2 it is decreased exponentially with time. Time constant for both transitions is approximately the same and equal to half an hour. The frequency drift occurs during 5 hours. The data listed in table II are for stable frequencies. The effect was not detected for halogen atoms.

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