^{35}Cl and ^{79}Br NQR Spectra in $Cp_2M\,Hal_2$

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The ^{35}Cl and ^{79,81}Br NQR spectra of $(C_5H_5)_2M\,Hal_2$ (M = Ti, Mo, W, Zr, Hf; Hal = Cl, Br) are similar. They are quadruplets with splittings ranging from 2 to 7%. The averaged frequencies of chlorine and bromine are related by a linear dependence. The temperature dependence of ^{81}Br in Cp_2HfBr_2 (in the range of 77 ÷ 224 K) is of conventional character with frequencies slowly changing with temperature; phase transitions have not been observed.

Key words: NQR, ^{35}Cl, ^{79,81}Br, temperature dependence of NQR frequencies, cyclopentadienyl derivatives.

This paper is a continuation of our study of ^{35}Cl and ^{79}Br NQR spectra of dicyclopentadienyldihalides of Ti, Mo, W, Zr, Hf [1–4]. We have also studied the ^{81}Br NQR frequency temperature dependence in Cp_2HfBr_2. All spectra were studied on a pulse NQR spectrometer. The obtained data are listed in Tables 1 and 2. The NQR spectra of all compounds under study look similar. They are fairly close quadruplets with splittings ranged from 2 to 7%, which corresponds to two crystallographically independent molecules in general position. X-ray structures are known for Cp_2TiCl_2 [5, 6], Cp_2ZrCl_2 and Cp_2MoCl_2 [7]. The crystal structures of the other compounds have not been determined.

However, judging by the spectra one can assume that, for one, the dichloride and dibromide crystals of the same metal be isomorphous. Secondly, $Cp_2M\,Hal_2$ compounds, where M = Zr, Hf, Ti and Hal = Cl, Br, are isostructural at low temperatures. Quadruplet NQR spectra of ^{35}Cl and ^{79}Br in $Cp_2Zr\,Hal_2$ are in full agreement with the crystal structure where two crystallographically independent molecules are in general position in space group $P\bar{1}$, determined for Cp_2ZrCl_2 [7]. Cp_2HfCl_2 and Cp_2HfBr_2 must have the same structure. Dicyclopentadienyl titanium dichloride, Cp_2TiCl_2 is isostructural with Cp_2ZrCl_2 [5, 7].

The similar behavior of chlorine and bromine NQR frequencies for the whole series resulted in linear dependences between ^{35}Cl and ^{79}Br for analogous com-

Table 1. ^{35}Cl and ^{79}Br NQR Spectra in $Cp_2M\,Hal_2$ at 77 K.

M ν, MHz	Zr	Hf	Ti	Mo	W
^{35}Cl	8.583 [1,2]		11.764 [3]	16.875 [4]	17.723 [4]
	8.763		11.884	17.098	17.772
	8.788		12.028	17.273	17.804
	8.868		12.208	17.273	18.063
^{79}Br	71.794 [1]	76.84	93.33 [3]		139.810 [4]
	72.530	77.36	97.58		142.194
	74.158	79.14	97.81		143.130
	74.921	79.98	100.02		144.294

Table 2. Temperature dependence of ^{81}Br NQR frequencies in Cp_2HfBr_2.

T, K	ν, MHz	T, K	ν, MHz	T, K	ν, MHz
77	64.21	135.0	64.15	189.0	64.04
	64.66		64.61		64.51
	66.12		66.04		...
	66.82		66.60		66.28
88.9	64.19	145.2	64.14	201.2	64.01
	64.65		64.60		64.48
	66.11		66.01		...
	66.79		66.54		66.19
101.2	64.18	156.7	64.12	213.0	63.99
	64.63		64.58		64.45
	66.09		65.99		...
	66.74		66.49		66.10
113.8	64.17	167.8	64.09	224.5	63.97
	64.63		64.57		64.41
	66.08		65.97		...
	66.69		66.42		66.00
124.8	64.16	178.3	64.07		
	64.62		64.54		
	66.06		65.95		
	66.65		66.36		

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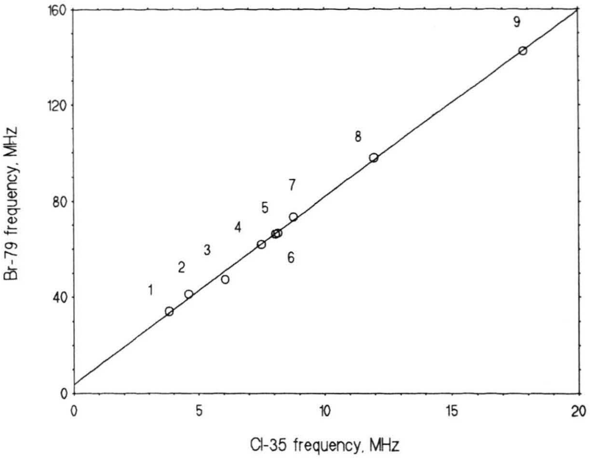

Fig. 1. Mutual dependence of ^{35}Cl and ^{79}Br NQR frequencies in Cp_nMHal_{4-n}. 1 and 4: $ZrHal_4$; 2 and 5: $HfHal_4$; 3: $TiHal_4$; 6: $CpTiHal_3$; 7: Cp_2ZrHal_2; 8: Cp_2TiHal_2; 9: Cp_2WHal_2.

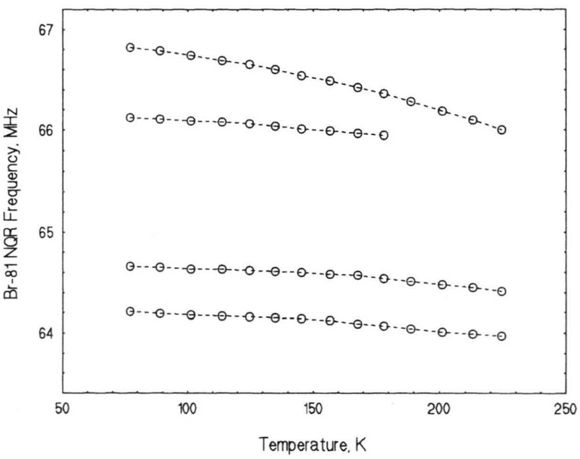

Fig. 2. Temperature dependence of ^{81}Br NQR frequencies in Cp_2HfBr_2.

pounds (see Figure 1). The same dependence is also valid for halogen frequencies in $CpTiHal_3$, $ZrHal_4$ and $HfHal_4$.

NQR frequencies averaged over crystalline splittings are related by the equations

$$v(^{79}\mathrm{Br}) = [3.808 + 7.784\, v(^{35}\mathrm{Cl})] \pm 1.06\ \mathrm{MHz}; \quad n = 9,\ r = 0.9989, \tag{1}$$

$$v(^{35}\mathrm{Br}) = [-0.469 + 0.128\, v(^{79}\mathrm{Br})] \pm 0.14\ \mathrm{MHz}; \quad n = 9,\ r = 0.9989. \tag{2}$$

The spectral lines of $ZrHal_4$ and $HfHal_4$, which are strongly split due to the intermolecular coordination interactions, were not included in the averaging, but compared separately (which explains nine dots for seven compounds on the plot, see Figure 1). Equations (1) and (2) allowed us to estimate unknown average NQR frequencies for $Cp_2Hf^{35}Cl_2$ (≈ 9.57 MHz) and $Cp_2Mo^{79}Br_2$ (≈ 137.15 MHz).

As we have noted earlier, the behavior of halogen NQR frequencies in cyclopentadienyl titanium halides is markedly affected by involving the halogen p_π-orbitals into bonding with the metal d-orbitals [3]. The latter, on one hand, results in an essential decrease in the halogen NQR frequencies of $TiCl_4$ (compared with expected ones in accordance with the titanium electronegativity), and, on the other hand, in their sharp increase with increasing Cp-ring number in Cp_nTiCl_{4-n} molecules. Recently we have observed a similar phenomenon while studying NQR spectra of zirconium cyclopentadienyl halides [8] in the series of mono- and bis(cyclopentadienyl) complexes. In these substances, despite a large variety of ligands attached to the metal atom, the NQR frequencies of the substance with one cyclopentadienyl ring are lower than those of that with two cyclopentadienyl rings. In this case we have not a large amount of experimental data. However, comparing the chlorine and bromine NQR frequencies in the series under study, we can observe that the less the p_π-halogen orbitals can be involved in the bonding with the transition element, the higher are the frequencies of respective compounds.

Earlier we have studied temperature dependences of halogen NQR frequencies in Cp_2TiCl_2, Cp_2ZrCl_2 and Cp_2ZrBr_2 [2]. For Cp_2TiCl_2 we observed a phase transition with a smooth multiplicity change, which is obviously related with a second order transition. We observed no phase transition in the temperature dependences of Cp_2ZrCl_2 and Cp_2ZrBr_2; the temperature changes are conventional, monotonous and weak. The temperature dependence of the ^{81}Br NQR frequency in Cp_2HfBr_2, given in Table 2 and Fig. 2 is similar; it is monotonous, with no phase transitions in the temperature range under study*. The temperature changes are conventional and small, more pronounced with the high frequency doublet.

Thus, the halogen NQR frequencies in Zr, Hf, Ti, Mo, W dicyclopentadienyl dihalides behave similarly; the chlorine and bromine frequencies in analogous compounds are related by a linear equation. However,

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* One of the lines was not detected above 178 K due to jamming.

the monotony in the frequency changes when moving from the top to the bottom of the Mendeleev table is not observed for the Ti-Zr-Hf series ($Zr < Hf < Ti$). In the same way, for derivatives of group VI ($Mo < W$).

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