On the estimation of the field constant of ^{35}Cl nuclear quadrupole resonance frequency in the series of $[R^1R^2R^3AsCl]^+M^-$ compounds

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The field constant of the NQR frequency of a chlorine atom (^{35}Cl) in a series of arsenic derivatives $[R^1R^2R^3AsCl]^+M^-$ was estimated from correlations. The field frequency is ~41.5±3.5 Hz cm kV^{-1}, which is nearly twice as much as that in analogous phosphorus compounds.

Key words: ^{35}Cl NQR spectra, field constant of NQR frequency, arsenic, correlation.

It is known[1] that the field constant of the NQR frequency $d\nu/dE_z$ of a chlorine atom (E_z is the electrostatic field intensity along the axis of the A—Cl bond) is highly characteristic and is determined only by the nature and state of a partner atom. This parameter is independent of the nature and number of substituents in the molecule for the given type of the bond. The field constant characterizes the polarizability of a resonance atom and enables one to estimate the easiness of the electron density redistribution under the field effect. Previously,[2] the field constants of NQR frequencies of a chlorine atom bound to the tetracoordinate phosphorus atom in a series of acid chlorides of oxygen, thio, and selenium acids of pentavalent phosphorus and in ionic compounds of the $[R^1R^2R^3PCl]^+M^-$ type have been estimated using the correlations. The isoelectronic series $R^1R^2P(O)Cl$ and $R^1R^2R^3SiCl$ were used as references for comparison.[2] It turned out that $d\nu/dE_z$ for compounds of the mentioned series changes as follows:

$$P(O)Cl \approx (RO)P(S)Cl > P(S)Cl > P(Se)Cl \geq PCl_{ion}.$$

The experimental data given in Table 1 and Fig. 1 made it possible to perform similar estimations for a series of chlorine derivatives of arsenic $[R^1R^2R^3AsCl]^+M^-$. If the linear correlation $\nu_{As-Cl} = \nu_0 + k\nu_{A-Cl}$ obeys, then its differentiation with respect to the electric field intensity E_z gives a correlation of the type

$$d\nu_{As-Cl}/dE_z = k d\nu_{A-Cl}/dE_z. \quad (1)$$

When the field constant $d\nu_{A-Cl}/dE_z$ is known, then the desired field can easily be estimated using the k coefficient. We used similar dependences for the ionic forms of the arsenic derivatives $[R^1R^2R^3AsCl]^+M^-$ and an $R^1R^2R^3GeCl$ series (see Fig. 1), because these compounds are isoelectronic and have similar tetrahedral configurations. In addition, the field constant was experimentally

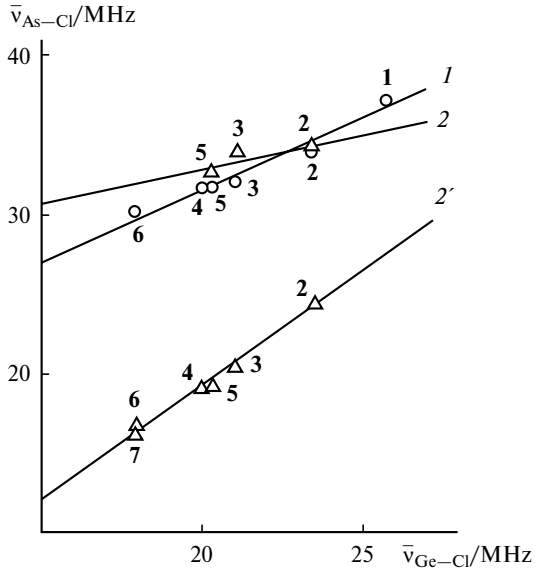

Fig. 1. Correlation of the ^{35}Cl NQR frequencies in the ionic (*1*) and molecular (*2*) arsenic compounds $[R^1R^2R^3AsCl]^+M^-$ and $R^1R^2R^3AsCl_2$, respectively, and the frequencies of the germanium derivatives $R^1R^2R^3GeCl$; (*2*) ν_{eq} and (*2′*) ν_{ax}.

Compound	R^1	R^2	R^3	Compound	R^1	R^2	R^3
1	Cl	Cl	Cl	**5**	Me	Me	Cl
2	Ph	Cl	Cl	**6**	Me	Me	Me
3	Ph	Ph	Cl	**7**	Et	Et	Et
4	Ph	Ph	Ph				

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Table 1. ^{35}Cl NQR spectra at 77 K (ν/MHz) for ionic and molecular forms of the arsenic derivatives $[R^1R^2R^3AsCl]^+M^-$ and $R^1R^2R^3AsCl_2$ and isoelectronic germanium and phosphorus derivatives

R^1	R^2	R^3	$[R^1R^2R^3AsCl]^+M^-$			$R^1R^2R^3AsCl_2$, ν_{As-Cl}				$R^1R^2R^3GeCl$,		$[R^1R^2R^3PCl]^+M^-$			Ref.*
			M^-	ν_{As-Cl}		ν_{eq}		ν_{ax}		ν_{Ge-Cl}		M^-	ν_{P-Cl}		
				ν_{exp}	$\bar{\nu}$	ν_{exp}	$\bar{\nu}$	ν_{exp}	$\bar{\nu}$	ν_{exp}	$\bar{\nu}$		ν_{exp}	$\bar{\nu}$	
Cl	Cl	Cl	$[AlCl_4]^-$	37.03 36.82	36.92	—	—	—	—	25.745 25.735 25.715 25.450	25.66	Cl^-	32.275	32.27	3, 4
Ph	Cl	Cl	$[BCl_4]^-$	34.32 33.94	34.13	34.66 34.18	34.42	24.92 24.00	24.46	23.430 23.410 23.105	23.32	$[SbCl_6]^-$	31.03	31.03	3, 5, 6
Ph	Ph	Cl	$[BCl_4]^-$	32.86 31.53	32.20	34.00	34.00	20.375 20.310	20.34	21.528 20.412	20.97	$[PCl_6]^-$	30.53 29.95	30.24	3, 5, 6
Ph	Ph	Ph	$[BCl_4]^-$	31.78	31.78	—	—	19.25 18.80	19.02**	19.89	19.89	$[SbCl_6]^-$	29.98 29.86	29.92	3—6
Me	Me	Cl	$[ICl_2]^-$	31.85	31.85	32.66	32.66	19.420 18.915	19.17	20.320 20.180	20.25	Cl^-	29.88	29.88	3, 4, 6, 7
Me	Me	Me	$[BCl_4]^-$	30.26	30.26	—	—	16.67	16.67	17.919	17.92				4—6
Et	Et	Et	—	—	—			16.36 16.15	16.25	17.850	17.85				6, 7

* The NQR spectra are taken in part from literature.[2]

** The NQR frequency of $^{75}As\ Ph_3AsCl_2$ at 77 K is 119.86 MHz.

determined for the chlorine atom at the germanium atom.[2,6] The following correlation was obtained by the least-squares method:

$$\nu_{[AsCl]^+} = (14.82 + 0.84\nu_{GeCl})\pm0.28\ \text{MHz}$$

$$(n = 6,\ r = 0.99). \qquad (2)$$

$d\nu_{[AsCl]^+}/dE_z = 41.2\pm2.5$ Hz cm kV^{-1}. The reference value $d\nu_{GeCl}/dE_z = 49\pm2$ Hz cm kV^{-1} was found experimentally.[1]

It is of interest that the earlier[2,6] estimates gave an almost halved value of the field constant of the chlorine atom at the phosphorus atom in a similar series $[R^1R^2R^3PCl]^+M^-$, namely, ~20±1.5 Hz cm kV^{-1}. Based on this fact, we can assume that the polarizability of the chlorine atom in the ionic arsenic derivatives is much higher than that of the phosphorus analogs. Only the appearance of the oxygen atom at the phosphorus atom in compounds $R^1R^2P(O)Cl$ increases sharply the field constant[3] to ~50±4 Hz cm kV^{-1}.

As it should be expected, the ^{35}Cl NQR frequencies in the ionic compounds of arsenic and phosphorus are related by a linear function

$$\nu_{[AsCl]^+} = (-33.33 + 2.17\nu_{[PCl]^+})\pm0.11\ \text{MHz}$$

$$(n = 5,\ r = 0.997). \qquad (3)$$

The experimental frequency values were taken from literature.[2–7] The value of the coefficient at $\nu_{[PCl]^+}$ in Eq. (3) also indicates that similar field effects in analogous compounds result in a stronger field response of the chlorine atom at the arsenic atom than that of Cl at the phosphorus atom.

A extensive experimental material made it possible to compare the behavior of the ^{35}Cl NQR frequencies in the ionic and molecular compounds of pentavalent arsenic. The plot of the NQR frequencies for these compounds *vs.* frequencies of the germanium derivatives is shown in Fig. 1. Since the molecular compounds, unlike the ionic compounds, have trigonal bipyramidal structures[8] and the chlorine atoms are localized in both the axial and equatorial positions, this plot is divided into two branches: equatorial and axial. Within the studied series of compounds, the NQR frequencies of the equatorial atoms lie higher than those of the axial atoms, which corresponds to a higher electron density in the axial position. At the same time, the slope ratios of these straight lines differ. For the lower-frequency axial atoms, the slope ratio is larger than that for the equatorial atoms. Using this plot, the hypothetical ^{35}Cl NQR spectrum at 77 K for $AsCl_5$ can be estimated: $\nu_{eq} = 35.0$ MHz and $\nu_{ax} = 27.7$ MHz. A similar relation is observed for the molecular and ionic phosphorus compounds (Fig. 2). It seems natural to expect that a more extensive experimental material for the phosphorus derivatives would confirm that the plot presented in Fig. 1 for the arsenic compounds is real. In this case, the silicon derivatives $R^1R^2R^3SiCl$ were used as the reference series.

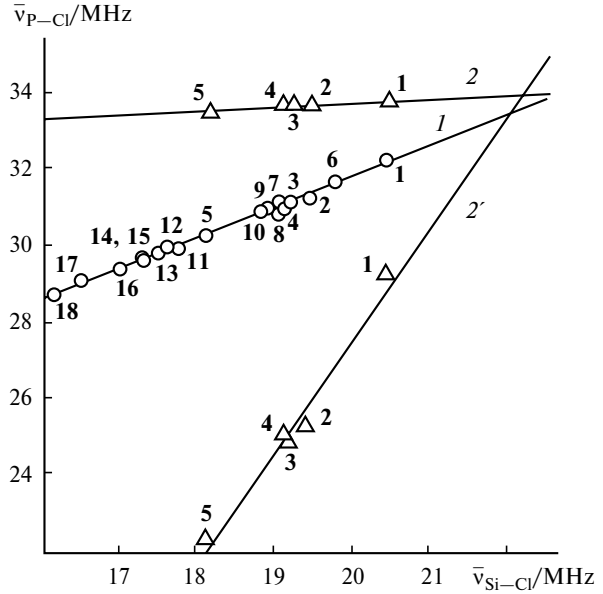

Fig. 2. Correlation of the ^{35}Cl NQR frequencies in the ionic (*1*) and molecular (*2*) phosphorus compounds $[R^1R^2R^3PCl]^+M^-$ and $R^1R^2R^3PCl_2$, respectively, and the frequencies of the silicon derivatives $R^1R^2R^3SiCl$; (*2*) ν_{eq} and (*2′*) ν_{ax}.

Compound	R^1	R^2	R^3	Compound	R^1	R^2	R^3
1	Cl	Cl	Cl	**10**	Et	Cl	Cl
2	*p*-ClC_6H_4	Cl	Cl	**11**	Me	Me	Cl
3	*p*-MeC_6H_4	Cl	Cl	**12**	Ph	Ph	Ph
4	Ph	Cl	Cl	**13**	Et	Et	Cl
5	Ph	Ph	Cl	**14**	Pr^i	Pr^i	Cl
6	F	Cl	Cl	**15**	Et	Ph	Ph
7	Me	Cl	Cl	**16**	Bu^t	Bu^t	Cl
8	*p*-MeC_6H_4	Cl	Cl	**17**	Me	Me	Me
9	Bu^t	Cl	Cl	**18**	Pr^i	Pr^i	Pr^i

All experimental data for these compounds are given in Ref. 2.

Thus, it can be assumed that for similar field effects in analogous compounds the electron density redistribution on the chlorine atom in the ionic arsenic compounds is stronger than that in the ionic phosphorus compounds.

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