# $^{121}$Sb and $^{35}$Cl NQR in RCN · SbCl$_5$ Complexes

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$^{35}$Cl and $^{121}$Sb NQR spectra of RCN · SbCl$_5$ complexes with R = Et, n-Pr, i-Pr, n-Bu, n-C$_5$H$_{11}$, Cl(CH$_2$)$_2$, C$_6$H$_4$CH$_2$, Ph, Cl, Me, CCl$_3$ were measured and/or refined at 77 K. Redistribution of the "transferred charge" in the SbCl$_5$ fragment of the complexes under study was investigated. The existence of a specific region of dispersion of the electron-nuclear motions (DENM) in RCN · SbCl$_5$ complexes was established.

*Key words:* Complexes RCN · SbCl$_5$, NQR, $^{121}$Sb, $^{35}$Cl, dispersion of the electron-nuclear motions (DENM).

## 1. Introduction

The dependence of the nuclear quadrupole coupling constant ($e^2Q\,q_{zz}$) on the ionization potential (I) of the oxygen lone pair in the antimony pentachloride complexes with oxygen containing ligands ($L_0$) has been shown to possess a logarithmic singularity in the vicinity of the energy of affinity to the electron of the antimony atom ($I_0$) of the rearranged Cl$_5$Sb fragment [1]. This singularity is determined by energy fluctuations ($\Delta I$) in the vicinity of $I_0$ neighborhood.

Additionally, energy fluctuations, $\Delta I$, predetermine the shape fluctuations of the electron density distribution at the antimony atom in the complex, which can be specified by the asymmetry parameter ($\eta$) of the electric field gradient (EFG) tensor $\eta = |(q_{xx} - q_{yy})/q_{zz}|$, i.e. $\Delta I \cong \Delta\eta$.

One finds the general form of dependence $\eta = \eta\,(e^2Q\,q_{zz})$ using a known approximate equation

$$\partial\eta = \frac{\mathrm{d}\eta}{\mathrm{d}q_{zz}}\,\partial q_{zz}. \tag{1}$$

Assuming $\partial\eta = (\eta_0 - \eta)$ and $\partial q_{zz} = (q_{zz} - q_{zz0})$ and solving (1) as a differential equation with separable variables, after some transformations one gets

$$(e^2Q\,q_{zz} - e^2Q\,q_{zz0}) \cdot (\eta_0 - \eta) = B\,\delta. \tag{2}$$

Equation (2) is valid if $B$ is a constant and $\delta = \pm 1$ ($e^2Q\,q_0$ and $\eta_0$ are at the origin). If the fluctuation spectrum is assumed to be continuous or rectangular, one can perform a simple integrated averaging for $e^2Q\,q_{zz}$ observed:

$$e^2Q\,q_{zz} = \frac{1}{2\Delta\eta}\int_{(\eta-\Delta\eta)}^{(\eta+\Delta\eta)}\left[e^2Q\,q_0 + \frac{B\cdot\delta}{(\eta_0-\eta)}\right]\mathrm{d}\eta$$
$$= e^2Q\,q_0 + \frac{B\cdot\delta}{2\Delta\eta}\ln\left|\frac{\eta-(\eta_0+\Delta\eta)}{\eta-(\eta_0-\Delta\eta)}\right|. \tag{3}$$

In the interval $\eta_0 \pm \Delta\eta$,

$$\left|\frac{(\eta-\eta_0)}{\Delta\eta}\right| = \mathrm{th}\left|\frac{\Delta\eta}{B}(e^2Q\,q_{zz} - e^2Q\,q_0)\right|. \tag{4}$$

Here $\Delta\eta$ is the depth of the fluctuation modulation; $e^2Q\,q_{zz}$ is the average value of the maximum EFG component along the Cl$_{ax}$ – Sb ... N – R axis corresponding to its observed value. To corroborate the validity of (3) there were studied $^{121}$Sb NQR spectra of RCN · SbCl$_5$ complexes, where most derivatives belonged to the alkyl series.

## 2. Experimental

The NQR spectra of antimony and chlorine in the RCN · SbCl$_5$ complexes were merely known for substances with R = Me, Cl, Ph, CCl$_3$ [2–5]. We remeasured those spectra (except the complex with R = CCl$_3$) to refine the data obtained earlier. Additionally, spectra of RCN · SbCl$_5$ complexes with R = Et, n-Pr, i-Pr, n-Bu, n-C$_5$H$_{11}$, Cl(CH$_2$)$_2$ and C$_6$H$_4$CH$_2$ were measured for the first time. The $^{35}$Cl NQR spectrum for the n-C$_3$H$_7$ · SbCl$_5$ complex was also measured. All experiments were carried out at

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Table 1. $^{121}$Sb NQR spectral parameters of RCN · SbCl$_5$ complexes at 77 K.

| NN | R | $e^2Qq_{zz}$, MHz | $\eta$, % |
|---|---|---|---|
| 1 | n-$C_5H_{11}$ | 179.874 | 12.12 |
| 2′ | $C_2H_5$ | 183.267 | −0.2 |
| 2″ | $C_2H_5$ | 187.085 | 9.3 |
| 3 | $Cl(CH_2)_2$ | 210.838 | 9.0 |
| 4 | i-$C_3H_7$ | 193.119 | 8.0 |
| 5 | $CH_3$[a] | 216.270 | 2.9 |
| 6 | n-$C_4H_9$ | 179.180 | 2.07 |
| 7 | Cl[a] | 235.930 | 1.15 |
| 8 | $C_6H_4CH_2$ | 184.176 | −0.6 |
| 9 | $C_6H_5$[a] | 174.230 | 0.825 |
| 10 | $Cl_3C$[b] | 199.64 | 36.0 |

[a] Our refined data. [b] Data from [4].

Table 2. $^{35}$Cl NQR spectra of RCN · SbCl$_5$ complexes at 77 K.

| NN | R | $\nu_{ax}$ MHz | $\nu_{eq}$ MHz | Ref. |
|---|---|---|---|---|
| 1 | n-$C_5H_{11}$ | 25.591 | 26.006<br>26.067<br>26.213<br>26.379 | a |
| 2′ | $C_2H_5$ | 26.683 | 25.645<br>25.659<br>25.885<br>25.885 | a |
| 2″ | $C_2H_5$ | 26.156 | 25.744<br>25.796<br>26.066<br>26.105 | |
| 3 | $Cl(CH_2)_2$ | 26.770 | 25.389<br>26.230 | a |
| 4 | i-$C_3H_7$ | 25.512 | 25.934<br>25.934<br>26.286<br>26.447 | a |
| 5 | $CH_3$ | 24.99 | 26.37 | [2] |
| 6 | n-$C_4H_9$ | 25.739 | 25.914<br>25.944<br>26.072<br>26.194 | a |
| 7 | Cl | 25.425 | 26.392<br>26.895 | [3] |
| 8 | $C_6H_4CH_2$ | 25.991 | 26.206<br>26.333<br>26.569<br>26.569 | a |
| 9 | $C_6H_5$ | 26.641 | 26.011<br>26.123 | [5] |
| 10 | n-$C_3H_7$ | 26.46 | 25.47<br>25.58<br>26.08<br>26.15 | a |

[a] This work.

77 K using an ISSh-2-13 pulse NQR spectrometer. The accuracy in measuring spectral line centers was ≈ 3 kHz for Cl and ≈ 5 kHz for Sb.

## 3. Results and Discussion

In accordance with the obtained spectra we found a complex molecule to occupy one general or one special position in a crystal. The only exception is EtCN · SbCl$_5$; for this substance there are two crystallographically independent complex molecules in general position. $^{121}$Sb $e^2Qq_{zz}$ and $\eta$ values are listed in Table 1. $^{35}$Cl NQR spectra are given in Table 2. The assignment of the $^{35}$Cl NQR lines to the axial or equatorial molecular positions were made using the signal intensity ratios or temperature dependence of the $^{35}$Cl NQR frequencies. As is known [5], the $^{35}$Cl NQR signal for the axial chlorine atom is the last one to disappear with increasing temperature. There was also observed a characteristic shift of the $^{35}$Cl NQR frequency for the side chain chlorine atom in the Cl(CH$_2$)$_2$CN · SbCl$_5$ complex (from 34.11 MHz in Cl(CH$_2$)$_2$CN to 35.55 MHz in the complex).

### 3.1. $^{121}$*Sb NQR*

The relation between $^{121}$Sb $e^2Qq_{zz}$ and $\eta$ for the complexes under study (see Fig. 1) was shown to be well described by an equation of type (3) with the following parameters: $e^2Qq_0 = 200.678$ MHz, $\eta_0 = 6.222\%$, $\Delta\eta = 4.894\%$ and $B = 85.795$ MHz%. In Fig. 2 $e^2Qq_{ii}$ $(i = x, y)$ is plotted against $e^2Qq_{zz}$; solid lines $(\delta = +1)$ and dashed lines $(\delta = -1)$ are solutions of (3); dots are experimental data. From the intersection of the curves with line $\eta = 0$ in Fig. 2 it follows that the $x$ and $y$ axes should be changed (since according to the definition $|q_{xx}| < |q_{yy}| < |q_{zz}|$), which is tantamount to the sign change of $\eta$ (see Fig. 1 and the relevant column in Table 1). As is seen from Fig. 1, five points for complexes with R = Me, Et, i-Pr, n-Bu and Cl(CH$_2$)$_2$ are in the region $(\eta_0 \pm \Delta\eta)$ and should be considered as dynamic ones. The nature of fluctuations, which reflects the existence of a specific $(\eta_0 \pm \Delta\eta)$ region, can be understood if we consider the following model.

1. If the electron density distribution on the antimony atom can possess several plausible configurations corresponding to the relevant potential wells, then transitions between those configurations might be tunnelling [6].

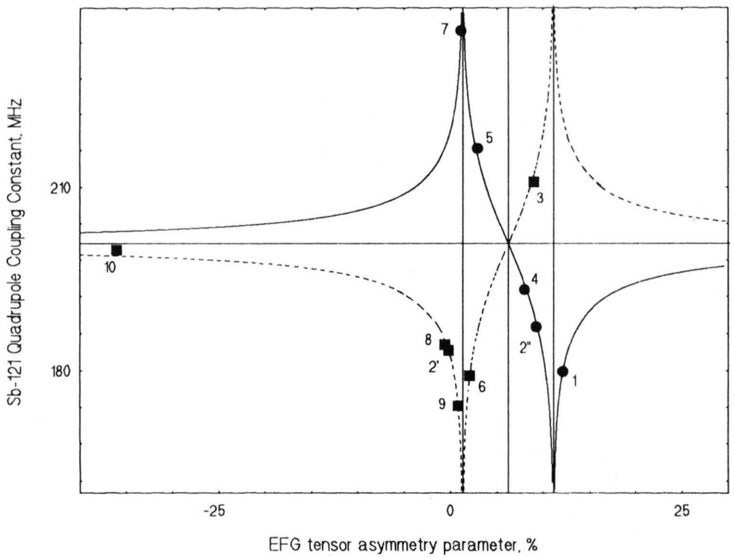

Fig. 1. Dependence of $e^2Qq_{zz}$ on the EFG asymmetry parameter [see (3)]. Notations are the same as in Table 1.

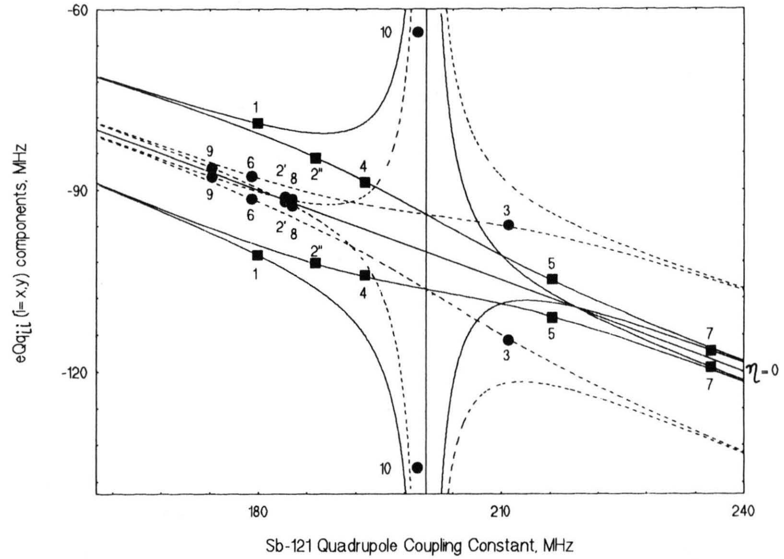

Fig. 2. Dependence (3); coordinate axes $eQq_{ii}$ ($e^2Qq_{zz}$), $i = x, y$. Notations the same as in Table 1.

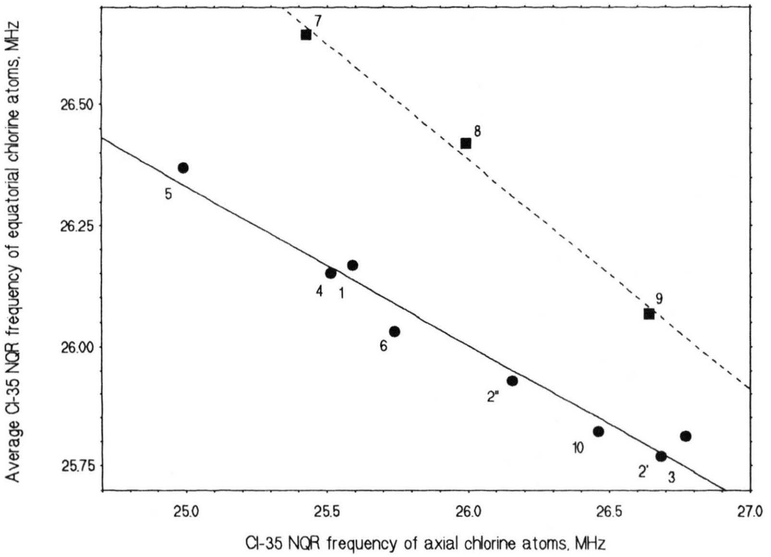

Fig. 3. Dependence $\bar{\nu}_{\mathrm{eq}}(\nu_{\mathrm{ax}})$. Notations the same as in Table 2. ——: see (9); - - -: see (10).

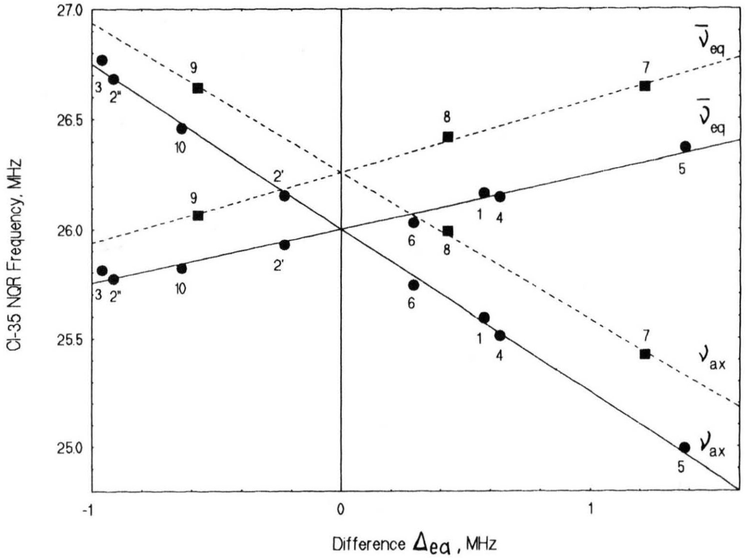

Fig. 4. Dependence $\nu_{\mathrm{ax}}$ and $\bar{\nu}_{\mathrm{eq}}$ on their difference $\Delta_{\mathrm{ea}} = \bar{\nu}_{\mathrm{eq}} - \nu_{\mathrm{ax}}$. Notations the same as in Table 2. ——: see (12) and (13); - - -: see (14) and (15).

2. This will, except for a resonance tunnelling, result in an essential increase in the correlation time (by $10^5 \div 10^{10}$ times) of the complete electron transfer upon tunnelling [7], which in its turn might bring the speeds of the electron motion into the region of characteristic speeds of the atomic nuclei motions.

3. The stochastic character of mutual motions of nuclei and electrons taking part in nonlinear vibrational motions is responsible for an additional mechanism for the EFG tensor averaging [8].

One can make an attempt to roughly estimate the characteristic times of the tunnel electron transfer. Since relative changes in the asymmetry parameter, $(\eta - \eta_0)/\Delta\eta$, and the average dynamic dipole moment, $\bar{\mu}$, with changing configurational electron distribution are due to the same reasons, it is natural to expect that

$$\bar{\mu} \sim (\eta - \eta_0)/\Delta\eta . \tag{5}$$

However, according to [9]

$$\bar{\mu} \sim \mathrm{th}\,|\delta E/kT|, \tag{6}$$

where $\delta E$ is the tunnel (inversion) splitting of the principal electron term. Then, comparing (4) and (6) we get

$$\delta E = \left| \frac{\Delta\eta}{B} (e^2 Q q_{zz} - e^2 Q q_0) k T \right| = \delta E_0 \left| \frac{e^2 Q q_{zz}}{e^2 Q q_0} - 1 \right| . \tag{7}$$

Changes in $\delta E$ and the correlation time of the complete electron transfer, $\tau$, are related by [7]

$$\tau = \frac{\pi\hbar}{\delta E} = \tau_0 \left| \frac{e^2 Q q_{zz}}{e^2 Q q_0} - 1 \right|^{-1} . \tag{8}$$

The $\tau$-values for the above five indicated complexes, whose quadrupole coupling constants are in the $(\eta_0 \pm \Delta\eta)$ region in Fig. 1, correspond to characteristic times of the atomic nuclei motions ($10^{-10} \div 10^{-14}$ sec).

### 3.2. $^{35}$*Cl NQR*

Redistribution of the so called "transferred charge" in the SbCl$_5$ fragment of the antimony pentachloride complexes under study is of essential interest. In the $^{35}$Cl NQR spectra of these complexes one can unambiguously assign NQR frequencies to axial ($\nu_{ax}$) or equatorial ($\nu_{eq}$) chlorine atoms (see Table 2). It also appeared to be possible to obtain a correlation equation relating changes in $\nu_{ax}$ and $\bar{\nu}_{eq}$ (here $\bar{\nu}_{eq}$ is the arithmetic average over observed frequencies in the multiplet), whose graphical solution is depicted in Figure 3. In this case the spectra of the EtCN · SbCl$_5$ complex are represented by two sets of lines considered separately.

For the series R = Alk (to the exclusion of the CCl$_3$ point) there was found the equation

$$\bar{\nu}_{eq} = (34.427 - 0.324\,\nu_{ax}) \pm 0.03 \text{ MHz}; \quad n = 7,\ r = 0.98. \tag{9}$$

For three other points (R = Ph, C$_6$H$_4$CH$_2$, Cl), an estimate is

$$\bar{\nu}_{eq} = (38.766 - 0.476\,\nu_{ax}) \pm 0.02 \text{ MHz}; \quad n = 3,\ r = 0.996. \tag{10}$$

As follows from (9) and (10), the charge redistribution along the axial and equatorial directions is inversely proportional, charge density changes on the equatorial atoms being 2–3 times smaller than those on the axial ones and opposite in sign. One comes to analogous conclusions when considering the dependence of $\bar{\nu}_{eq}$ and $\nu_{ax}$ on their difference $\Delta_{ea} = \bar{\nu}_{eq} - \nu_{ax}$ (see Fig. 4):

$$\nu = \nu_0 + K\,\Delta_{ea}, \tag{11}$$

where $\nu_0$ is referred to a hypothetical complex with $\nu_{ax} = \bar{\nu}_{eq}$.

For the alkyl series, the equations relating $\bar{\nu}_{eq}$ and $\nu_{ax}$ to $\Delta_{ea}$ are

$$\nu_{ax} = (26.004 - 0.753\,\Delta_{ea}) \pm 0.025 \text{ MHz}; \quad n = 7,\ r = 0.999, \tag{12}$$

$$\bar{\nu}_{eq} = (26.004 + 0.246\,\Delta_{ea}) \pm 0.025 \text{ MHz}; \quad n = 7,\ r = 0.990. \tag{13}$$

Estimated values for the series Cl, C$_6$H$_4$CH$_2$ and Ph are

$$\nu_{ax} = (26.261 - 0.677\,\Delta_{ea}) \pm 0.013 \text{ MHz}; \quad n = 3,\ r = 0.9996, \tag{14}$$

$$\bar{\nu}_{eq} = (26.261 - 0.323\,\Delta_{ea}) \pm 0.013 \text{ MHz}; \quad n = 3,\ r = 0.9983. \tag{15}$$

## 4. Conclusions

As is seen from (1), maximum change in the increment of $\Delta e^2 Q q_{zz} = (e^2 Q q_{zz} - e^2 Q q_0)$ must occur at $\eta_0$, which corresponds to the maximum charge separation between the donor and acceptor parts of the complex. A recharging between the complex parts must occur after passing the $\eta_0$ point.

However, as follows from (3), the "recharging" mechanism differs from a simple sign change of the SB ... N induced coordination bond dipole. The "recharging" does not begin at $\eta_0$, but at $(\eta_0 - \Delta\eta)$. Near this point, inside the $(\eta_0 \pm \Delta\eta)$ area, there occurs a levelling of the charges localized on the atoms participating in the Sb ... N coordination bond, so that the additional gradient, $\Delta e^2 Q q_{zz} = (e^2 Q q_{zz} - e^2 Q q_0)$, at $\eta_0$ becomes zero. In the interval $\eta_0 \div (\eta_0 + \Delta\eta)$, $\Delta e^2 Q q_{zz} = (e^2 Q q_{zz} - e^2 Q q_0)$ gradually increases, but is opposite in sign.

The whole process is accompanied by efficient dynamic motions, since characteristic correlation times of atomic and electron motions overlap upon tunnelling.

As there are obviously more than two, deformational motions in the octahedral complexes, we have to do with stochastic dynamics of a set of vibration systems, which, in general, are not linear. The latter results in either a continuous or a rectangular spectrum of low frequency vibrations of the electron-nuclear systems. That is why (3) has such a good descriptive ability.

Thus, there has been established the existence of a specific region where Born-Oppenheimer rules are violated and which can be called the region of dispersion of the electron-nuclear motions (DENM) in RCN · $SbCl_5$ complexes.

The existence of the DENM region must result in anomalies in the chemical behavior of both parts of the complex which, first of all, bring about a sharp change in the energetics of chemical reactions proceeding with participation of these complexes.

[1] G. K. Semin, Abstr. XIth Inter. Symposium NQR, London, England, 1991, p. PII: 32.

[2] R. F. Schneider and J. V. DiLorenzo, J. Chem. Phys. **47,** 2343 (1967).

[3] M. Burgard and E. A. C. Lucken, J. Mol. Struct. **14,** 397 (1972).

[4] M. Mishima, J. Sci. Hiroshima Univ. Ser. A. Math. Phys. Chem. **46,** 41 (1982).

[5] J. Rupp-Bensadon and E. A. C. Lucken, J. Chem. Soc. Dalton Trans. N**3,** 19 (1983).

[6] I. B. Bersuker, Effect Jahna-Tellera i vibronnye vzaimodejstvija v sovremennoj khimii. Moscow 1987 (in Russian).

[7] E. O. Kein, in: Tunnelling Phenomena in Solids. New York 1969, pp. 9–19.

[8] B. V. Chirikov, Uspekhi Fizicheskikh Nauk **105,** 7 (1971) (in Russian).

[9] I. B. Bersuker, Teoreticheskaya i eksperimental'naya khimiya **5,** 293 (1969) (in Russian).