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1964

SovietRxiv

Abstract

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PHYSICAL CHEMISTRY

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ON NUCLEAR QUADRUPOLE RESONANCE IN POLYMERS

(Presented by Academician A. N. Nesmeyanov, 10 VI 1964)

It was shown earlier by one of us (^1) that the NQR frequency of a halide (Br^79 or Cl^35) attached to a polyhalogen-substituted aliphatic chain can be calculated from the following empirical formula

$$\nu_{\mathrm{I}} = \nu_{0\mathrm{I}} + \Delta_1 \nu \sum_n \xi^{n-1} \qquad (1)$$

for a halide at a primary carbon atom,

$$\nu_{\mathrm{II}} = \nu_{0\mathrm{II}} + \Delta_1 \nu \sum_n \xi^{n-1} \qquad (2)$$

at secondary, tertiary, etc., carbon atoms. In formulas (1) and (2), $\Delta_1 \nu$ is the primary shift. The primary shift is defined as the difference between the values of the mean limiting frequency $\nu_{0\mathrm{I}} = \mathrm{const}$ and the NQR frequencies of halides in compounds of the type Hal $(CH_2)_n$ Hal at $n = 1$.

$$\Delta_n \nu = \xi^{n-1} \Delta_1 \nu \qquad (3)$$

for the remaining n; ξ is the dimensionless attenuation coefficient for transmission of the effect along a chain of carbon atoms ($\xi < 1$).

Comparison of calculated NQR frequencies for a large number of compounds with the experimental ones showed that there is fairly good agreement with experiment (deviation 0.1-2%)*.

The method described above was applied to the calculation of the NQR frequencies of Cl^35 in chlorine-containing chain polymers.

Using formula (2), we calculated the value of the NQR frequency of Cl^35 in polyvinylidene chloride, the monomer frequencies of which had previously been found by us (36.873; 36.524; 36.524 and 36.258 MHz, and averaged over nonequivalent crystal positions, 36.545 MHz).

The experimentally found NQR spectrum of Cl^35 of polyvinylidene chloride $(-CH_2-CCl_2-)_n$ contains two lines with a width at half height of ~ 300 kHz ($\nu_A = 38.04 \pm 0.05$ and $\nu_B = 37.25 \pm 0.05$ MHz, with a signal-to-noise ratio of $\sim 8 \div 10$) and one broad (~ 600 kHz) weak line (s/n $= 2 \div 3$) at about 36.6 ± 0.1 MHz**.

If one assumes that the chlorine atoms are crystallographically equivalent, and that the broad and weak line belongs to monomer residues, terminal groups, and low-molecular-weight fractions, then the remaining spectrum, consisting of two lines of approximately equal intensity, can be explained by only one repeating combination of monomer fragments

$$[-CH_2CCl_2CCl_2CH_2CCl_2CH_2CH_2CCl_2-]_m.$$

* In the calculations, for Cl^35 it was taken that $\nu_{0I} = 33.0$ MHz, $\nu_{0II} = 32.0$ MHz, $\Delta_1\nu = 2.4$ MHz and $\xi = 0.47$, and for Br^79 that $\nu_{0I} = 250.0$ MHz, $\nu_{0II} = 243.3$ MHz, $\Delta_1\nu = 22$ MHz, $\xi = 0.50$. All frequencies, both calculated and experimental, are given at 77°K.

** A study of crystal splittings in the NQR spectra of ordinary ordered molecular crystals, as well as of the line widths of the NQR lines of halogen atoms found by us in statistically partially disordered molecular crystals, showed that frequency shifts and line broadening arising from differences in the crystal field cannot exceed 2% of the measured frequency. This corresponds to equivalent quality factors of the NQR lines $Q_{\text{eqv}} = \nu/\Delta\nu_{1/2} \approx 50$. (It should be noted that by the usual, non-pulse, method one can observe lines with an equivalent quality factor of at least $Q_{\text{eqv}} \approx 5000$.)

Since the values of ξ^n rapidly decrease with increasing n, the contributions of terms containing high powers of ξ may be neglected; and for the frequencies of NQR of chlorine atoms located in two nonequivalent positions in the polyvinylidene chloride fragment of the structure given above, formula (2) takes the form:

$$\begin{aligned} \nu_A &= \nu_{0II} + \Delta_1\nu(1 + 2\xi + 2\xi^2 + 2\xi^3 + 2\xi^5 + 2\xi^6 \ldots) \cong 38.4 \text{ MHz}, \\ \nu_B &= \nu_{0II} + \Delta_1\nu(1 + 2\xi^2 + 4\xi^3 + 4\xi^5 + 2\xi^6 \ldots) \cong 37.0 \text{ MHz}. \end{aligned} \tag{4}$$

The deviations of the calculated frequency values from the experimental ones do not exceed the accuracy of the calculation and have a logical character: comparison of the calculated and experimental data for polyhaloethanes shows that in the absence of halides at the neighboring carbon atom the calculated frequencies are always somewhat lower than the experimental ones, whereas when there is a large number of halogen atoms at neighboring carbon atoms their experimentally obtained frequencies are always somewhat lower than the calculated ones. This is explained by spatial interactions of halogen atoms attached to neighboring carbon atoms.

The regularity found—(1) and (2)—was also used by us in determining the structure of the polymer fragment of the polymerization product of trichloropropene ($Cl_3C—CH = CH_2$). The NQR frequencies of Cl^{35} of the monomer are 38.476, 38.272, and 38.150 MHz, with an average frequency of $\sim$ 38.30 MHz.

Of the three proposed structures (1—containing trichloromethyl groups, 2—containing CCl_2 and CCl_3 groups, and 3—containing, after rearrangement, a fragment of the type $[-CH_2—CHCl—CCl_2-]_m$), the last was selected on the basis of the results of calculation and experiment.

The calculation was carried out analogously to the case of polyvinylidene chloride:

$$\nu_{\mathrm{CHCl}} = \nu_{0\mathrm{II}} + 2\Delta_1\nu(\xi + \xi^2 + \xi^3 + \xi^4 + \xi^5 + \xi^6 \ldots), \tag{5}$$

$$\nu_{\mathrm{CCl_2}} = \nu_{0\mathrm{II}} + \Delta_1\nu(1 + \xi + \xi^2 + 4\xi^3 + \xi^4 + \xi^5 + 4\xi^6 \ldots). \tag{6}$$

In this case the line $\nu_{\mathrm{CCl_2}} = 37.33$ MHz should be twice as intense as the line $\nu_{\mathrm{CHCl}} = 36.21$ MHz.

Experimentally, a very broad Cl^{35} NQR line was detected, with a linewidth at half-height of 1-1.5 MHz and a maximum at 37.01 ± 0.10 MHz (signal-to-noise ratio $\sim$ 3). The value of the average of the calculated frequencies (with allowance for weights) is 36.96 MHz; it agrees with the experimental value to an accuracy of $\sim$ 0.2%. It is evident that the experimentally found spectrum also consists of two broad merged lines, since its width exceeds the maximum possible in partially disordered molecular crystals (see above).

The calculations and measurements presented show that the NQR method, when a pulsed technique for detecting signals is used, can be employed to prove the structure of fragments of halogen-containing polymers.

However, the information obtained from NQR spectra on the structure of polymers may turn out to be substantially richer than that presented above when the temperature changes in the shape and structure of the line are analyzed. It may be hoped that the study of line shapes, relaxation times, and their temperature changes will make it possible to draw conclusions about the character and degree of order of polymer crystals, as well as about the forms of thermal motion of polymer molecules.

We consider it our duty to express gratitude to A. I. Kitaigorodskii for his attention to this work.

We express special appreciation to B. N. Pavlov and D. Ya. Shtern for providing the pulsed apparatus, and to G. S. Kolesnikov, A. M. Sladkov, and A. P. Suprun for providing the samples.

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Received
9 I 1964

CITED LITERATURE

1. G. K. Semin, DAN, 158, No. 4 (1964).

Note: Figure translations are in progress. See original paper for figures.

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