

Zeeman NQR Studies on Polycrystals of Copper Compounds, Arsenic Compounds, and Chlorine Compounds*

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Powder Zeeman NQR (PZNQR) spectra of ^{63}Cu , ^{75}As , and ^{35}Cl in various compounds have been observed at 77 K. On the basis of the types of simulated integral curves of PZNQR absorption, the estimated asymmetry parameters of the electric field gradients have been divided into three classes; (1) measurable, (2) small (smaller than about 0.05), and (3) very small (probably zero). The asymmetry parameters have been found to be very small (^{63}Cu , NQR frequency = 26.704 MHz) in Cu_2O ; 0.40 (^{63}Cu , 32.617 MHz) in $\text{KCu}(\text{CN})_2$; very small (^{75}As , 116.820 MHz) in As_2O_3 ; very small (^{75}As , 78.950; ^{35}Cl , 25.0567 and 25.4036 MHz) and small (^{35}Cl , 24.9581 MHz) in AsCl_3 ; very small (^{75}As , 98.501 and 99.046 MHz) in $\text{As}(\text{C}_6\text{H}_5)_3$; small (38.389 MHz), 0.15 (38.464 MHz), and 0.14 (38.503 MHz) for ^{35}Cl in hexachlorobenzene; small (35.847 MHz) and very small (39.154, 39.603, and 39.615 MHz) for ^{35}Cl in 1-chloro-2-(trichloromethyl)-benzene; small (32.619 MHz) and very small (32.878 MHz) for ^{35}Cl in 1,4-dichlorobutane; very small (37.828 and 38.051 MHz) for ^{35}Cl in 1,1,1-trichloroethane.

Introduction

Powder Zeeman NQR (PZNQR), in which resonance absorption curves were observed under weak magnetic field, was firstly reported by Toyama and Morino [1, 2]. Brooker and Creel, and other researchers investigated PZNQR experimentally and/or using simulation methods [3–11].

Because the asymmetry parameter (η) of the electric field gradient at a nucleus with spin $I = 3/2$ cannot be determined from the NQR frequency itself for a powder sample, the Zeeman effect on NQR for the single crystal has been usually examined. PZNQR is another useful method for the determination of η . The η values estimated from the PZNQR method sometimes give slightly larger values than the values determined by means of the NQR Zeeman method using single crystals because of the following three reasons: (1) the

frequency of an NQR oscillator may gradually drift in the repeated scanning time; (2) for a liquid compound at room temperature, there might be some single-crystal grains in a solidified sample at 77 K; (3) the intensity of the static magnetic field for the Zeeman effect may slightly decrease during the scanning time. In spite of these disadvantages, the PZNQR method has been adopted especially when single crystals are not available.

In a previous paper, we (O. E. and H. N.) have pointed out that the η values of Br in bromine compounds can be grouped into three classes on the basis of the patterns of integral curves of PZNQR [10]. First class (type 1): η is greater than about 0.05. For such η values, the PZNQR curve has two sharp dips at the lower- and higher-frequency sides of the central frequency of the resonance. Moreover, two small peaks exist at the mouth of the individual dip. Second class (type 2): η is small. In this case, a PZNQR curve has two small (sometimes broad) peaks which are located at the lower- and higher-frequency sides of the central position of the resonance. Third class (type 3): η is very small, probably zero. For this case, a PZNQR curve exhibits a shoulder-head-shoulder pattern, i.e., a bell

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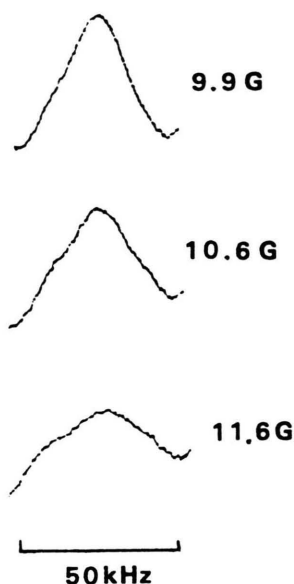


Fig. 1. PZNQR absorption curves of ^{63}Cu in Cu_2O .

shape on which a small bell overlies at the central frequency. In this work, we estimated η values by calculating numerically from observed data or by comparing shapes of observed PZNQR curves with those of simulated ones.

Experimental

Absorption curves of PZNQR were obtained by using a superregenerative oscillator of the modified Kushida type. To investigate the Zeeman effect of NQR curves, the static magnetic field was produced by a Helmholtz coil which was set coaxially with the NQR oscillation coil (sample coil). NQR signals were detected in integral form through a bridge circuit and were fed into a signal averager to improve the signal-to-noise ratio [9, 12]. Because the frequency of the NQR oscillator was modulated at a low sweep-speed, the frequency drift of the NQR oscillator placed a limit on the accumulation time of the signal averager. All the NQR measurements were made at 77 K. In order to compare with the observed PZNQR curves, computer simulated diagrams were obtained using a method similar to that of Brooker and Creel [5].

All chemicals were purchased from Wako Pure Chemical Industries, Ltd. or Nakalai Tesque Ltd., and used without further purification.

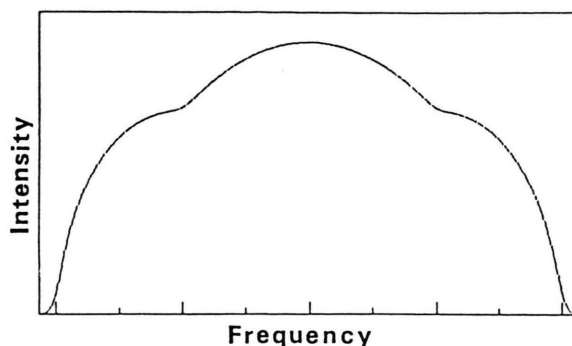


Fig. 2. Simulated absorption curve of PZNQR for $\eta = 0$.

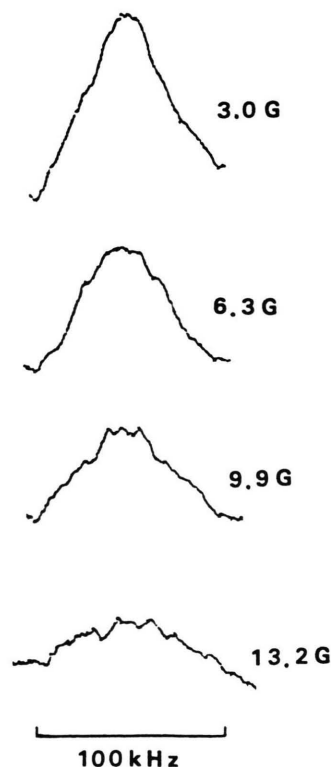
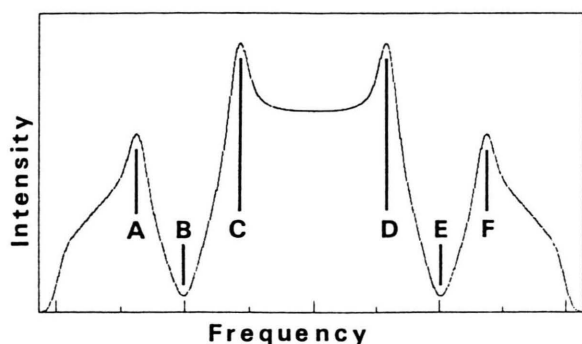


Fig. 3. PZNQR absorption curves of ^{63}Cu in $\text{KCu}(\text{CN})_2$.

Results and Discussions

Krüger and Meyer-Berkhout have studied the NQR of ^{63}Cu in Cu_2O at 87 K, and have given 26.697 MHz as the resonance frequency [13]. We observed the integral curves (line shapes) of PZNQR of ^{63}Cu in Cu_2O as a function of static magnetic field strength (Figure 1). For comparison, a simulated PZNQR curve for $\eta = 0$ (type 3) is shown in Figure 2.

Fig. 4. Simulated absorption curve of PZNQR for $\eta = 0.4$.Fig. 5. PZNQR absorption curves used to estimate η for $\text{KCu}(\text{CN})_2$.

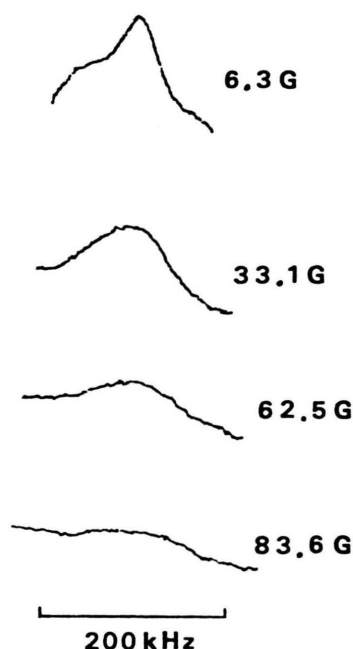
The observed curves show the characteristic pattern (shoulder-head-shoulder pattern) of type 3, indicating that the η value is very small (probably zero).

McKown and Graybeal investigated the NQR of ^{63}Cu in $\text{KCu}(\text{CN})_2$ by means of the Zeeman effect of a single crystal and obtained an η value of 0.78 ± 0.07 [14]. Figure 3 shows PZNQR curves of ^{63}Cu in $\text{KCu}(\text{CN})_2$. The PZNQR curve at 13.2 G resembles a simulated curve (type 1) for $\eta = 0.4$ shown in Figure 4. Consequently, we ascribe the PZNQR curve of ^{63}Cu in $\text{KCu}(\text{CN})_2$ to the type 1. From the observed curves as shown in Fig. 5, the η value can be estimated according to the following approximate equation valid for small η [9]:

$$\eta = \frac{(v_C - v_A) + (v_F - v_D)}{2(v_E - v_B)} = \frac{\overline{AC} + \overline{DF}}{2\overline{BE}}, \quad (1)$$

where v_A , v_B , v_C , v_D , v_E , and v_F are frequencies at points A, B, C, D, E, and F, and \overline{AC} , \overline{DF} , and \overline{BE} are the horizontal distance between the points A and C, and so forth. The resulting η is estimated to be 0.38. However, with increasing η , (1) becomes gradually inadequate. When η is large, the following equation, which is based on the peak points of the curve, should be adopted:

$$\eta = \frac{\overline{AC} + \overline{DF}}{\overline{AD} + \overline{CF}}, \quad (2)$$

Fig. 6. PZNQR absorption curves of ^{75}As in As_2O_3 (arsenolite).Fig. 7. PZNQR absorption curves of ^{75}As in AsCl_3 .

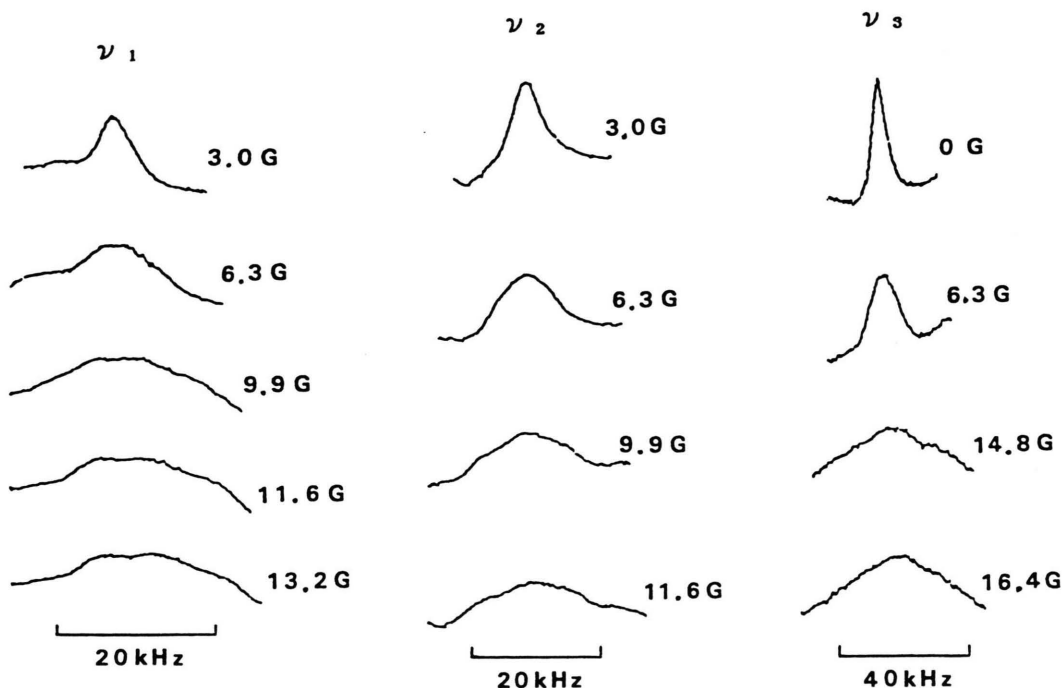


Fig. 8. PZNQR absorption curves of ^{35}Cl in AsCl_3 .

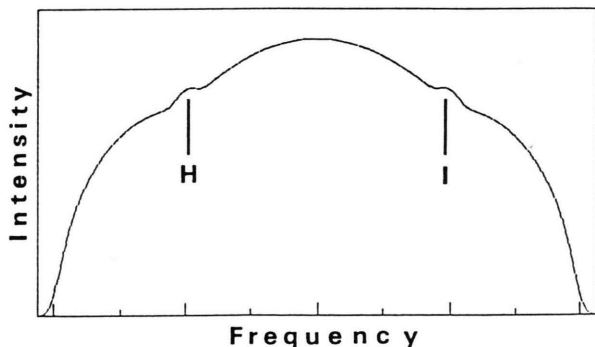


Fig. 9. Simulated absorption curve of PZNQR for $\eta = 0.02$.

where \overline{AD} and \overline{CF} are the horizontal distances, between A and D , and C and F , respectively. On the basis of (2), the η value is determined to be 0.40.

It is known that As_2O_3 exhibits polymorphism (arsenolite, claudetite I, and other phases). As the NQR frequency of ^{75}As in As_2O_3 at 77 K, Treacy and Taylor reported 116.820 and 112.321 MHz for arsenolite and claudetite I, respectively [15]. We obtained the PZNQR curves of arsenolite as shown in Figure 6. The PZNQR curves shown in Fig. 6 are of type 3.

The NQR of ^{75}As in AsCl_3 has been studied by Yusupov *et al.* [16]. The resonance frequency is 78.950

MHz at 77 K. Figure 7 shows PZNQR curves of ^{75}As in AsCl_3 . They are simply broadened with increasing magnetic field. Although a series of curves seems to be between types 2 and 3, we tentatively assign the η value of ^{75}As to type 3.

From the Zeeman NQR measurements of ^{35}Cl in AsCl_3 at 77 K, Litzistorf *et al.* gave the following results: $\nu_1 = 24.9581$ MHz, $\eta = 0.077 \pm 0.008$; $\nu_2 = 25.0567$ MHz, $\eta = 0.071 \pm 0.006$; $\nu_3 = 25.4036$ MHz, $\eta = 0.075 \pm 0.006$ [17]. We observed the three PZNQR lines due to ^{35}Cl (Figure 8). The appearance of the three ^{35}Cl lines indicates that, in the polycrystal, the three Cl atoms in a AsCl_3 molecule are inequivalent. As an example of small η , a computer simulation curve (type 2) for $\eta = 0.02$ is illustrated in Figure 9. It roughly resembles the observed curves at ν_1 , whereas the simulation curve (type 3) in Fig. 2 resembles the observed curves at ν_2 and ν_3 . Consequently $\eta(\nu_1)$, which represents the value at a Cl nucleus responsible for the absorption curve at ν_1 , is evaluated to be small, whereas $\eta(\nu_2)$ and $\eta(\nu_3)$ are evaluated to be very small.

For ^{75}As in $\text{As}(\text{C}_6\text{H}_5)_3$, the NQR frequencies have been determined to be 98.900 and 98.500 MHz at 77 K by Barnes and Bray [18]. Figure 10 shows PZNQR curves of ^{75}As in $\text{As}(\text{C}_6\text{H}_5)_3$. The observa-

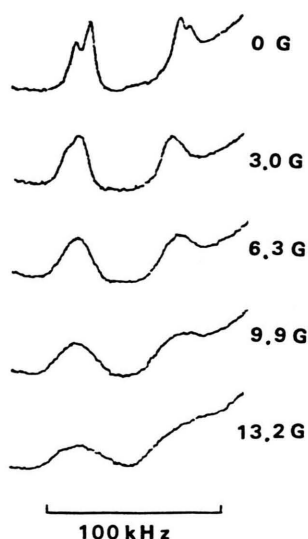
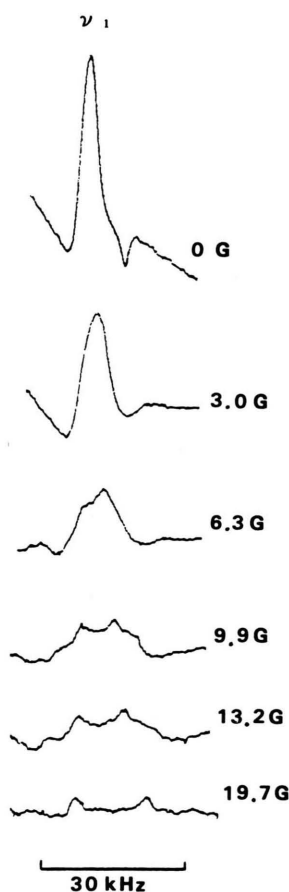
Table 1. Resonance frequencies, η values, and coupling constants (e^2qQh^{-1}) of copper compounds and arsenic compounds at 77 K.

Compound	Nu- cleus	Frequency (MHz)	η	e^2qQh^{-1} (MHz)
Cu_2O	^{63}Cu	26.704	very small	53.408
$\text{KCu}(\text{CN})_2$	^{63}Cu	32.617	0.40	63.561
As_2O_3	^{75}As	116.820 [15]	very small	233.640
AsCl_3	^{75}As	78.950 [16]	very small	157.900
	^{35}Cl	24.9581 [17]	small	49.916
	^{35}Cl	25.0567 [17]	very small	50.113
	^{35}Cl	25.4036 [17]	very small	50.807
$\text{As}(\text{C}_6\text{H}_5)_3$	^{75}As	98.501	very small	197.002
	^{75}As	99.046	very small	198.092

tion of two original lines of PZNQR indicates that in the polycrystal there are two different environments around As in $\text{As}(\text{C}_6\text{H}_5)_3$. Both the original two lines of PZNQR are split into two peaks, separated by about 7 kHz. As the magnetic field is strengthened, broadening of the two individual lines occurs, accompanied by the coalescence of the two peaks into a single line. Taking into account the shapes of the PZNQR curves, it is most likely that the η values for the two lines are very small.

Table 1 summarizes the resonance frequencies, the magnitudes of η , and the coupling constants for the copper and arsenic compounds examined. The coupling constants in Table 1 were calculated assuming $\eta = 0$ in small and very small cases.

NQR lines due to ^{35}Cl in hexachlorobenzene were observed at 38.389 (ν_1), 38.464 (ν_2), and 38.503 (ν_3) MHz. Since the three NQR lines have the same absorption intensity, the individual lines are identified to correspond to two Cl atoms. Consequently, in hexachlorobenzene there are three kinds of Cl atoms which are distinguishable on the basis of the NQR frequency. A monoclinic crystal of hexachlorobenzene has a bimolecular unit at room temperature [19]. Our finding that six Cl atoms in hexachlorobenzene are classified into three groups, each containing two Cl atoms, is consistent with the crystal structure of hexachlorobenzene. Figures 11, 12, and 13 show PZNQR curves for each absorption line due to ^{35}Cl in hexachlorobenzene as a function of magnetic field intensity. According to (1), $\eta(\nu_2)$ and $\eta(\nu_3)$ are calculated to be 0.15 and 0.14, respectively. These $\eta(\nu_2)$ and $\eta(\nu_3)$ values are in good agreement with η values of 0.151 ± 0.016 (at -78°C) determined by Richardson [20]. The curves in Fig. 11 are closely similar in shape to the simulated PZNQR curve (type 2) for $\eta = 0.02$ shown in Fig. 9,

Fig. 10. PZNQR absorption curves of ^{75}As in $\text{As}(\text{C}_6\text{H}_5)_3$.Fig. 11. PZNQR absorption curves at ν_1 for hexachlorobenzene.

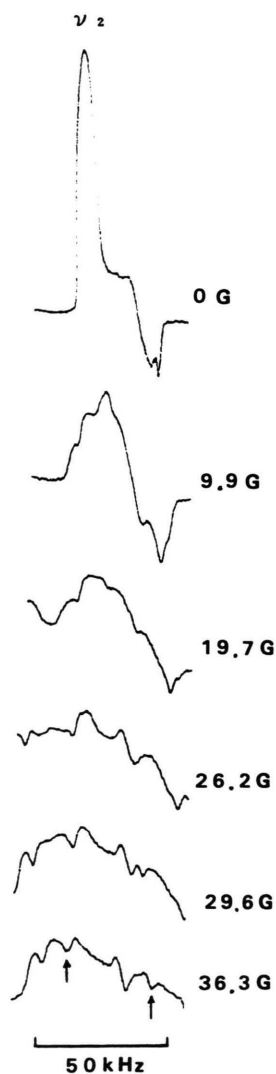


Fig. 12. PZNQR absorption curves at ν_2 for hexachlorobenzene. The arrows show the dips whose frequencies are used for calculation of the η value.

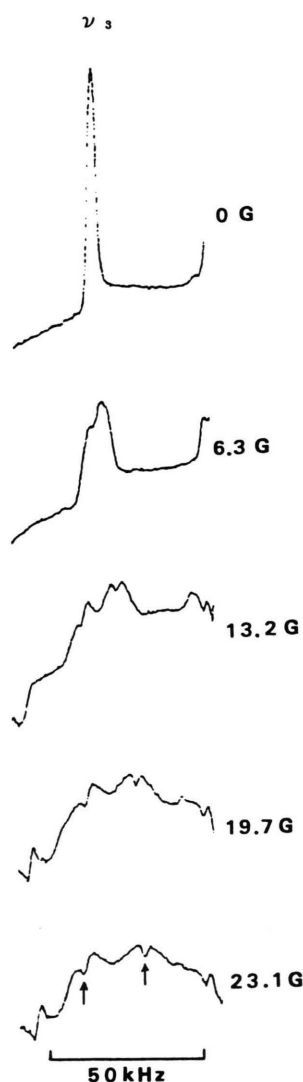


Fig. 13. PZNQR absorption curves at ν_3 for hexachlorobenzene. The arrows show the dips whose frequencies are used for calculation of the η value.

which exhibits two small peaks (H and I), indicating that $\eta(\nu_1)$ is small (about 0.02). Because $\eta(\nu_1)$ is significantly smaller than $\eta(\nu_2)$ and $\eta(\nu_3)$, the environment around the Cl atom responsible for ν_1 is apparently different from those for ν_2 and ν_3 .

1-Chloro-2-(trichloromethyl)-benzene exhibited four NQR lines at 35.796 (ν_1), 39.154 (ν_2), 39.603 (ν_3), and 39.615 (ν_4) MHz. PZNQR curves at ν_1 and those at higher frequencies are shown in Figs. 14 and 15, respectively. Since the PZNQR curve at ν_1 in Fig. 14 resembles the pattern of type 2, $\eta(\nu_1)$ is estimated to be

small. From the spectral similarity between the simulated curve in Fig. 2 and the observed PZNQR curve at ν_2 in Fig. 15, $\eta(\nu_2)$ is estimated to be very small. The curves at ν_3 and ν_4 in Fig. 15 become broad with increasing intensity of the Zeeman magnetic field. In the broadening process, the positions of the central peaks remain unaltered though the two shoulders, respectively assigned to the curve at ν_3 and that at ν_4 , overlap. These curves seem to indicate type 3. Thus, we estimate the $\eta(\nu_3)$ and $\eta(\nu_4)$ to be very small. Both the fact that ν_1 is the lowest of the frequencies and the

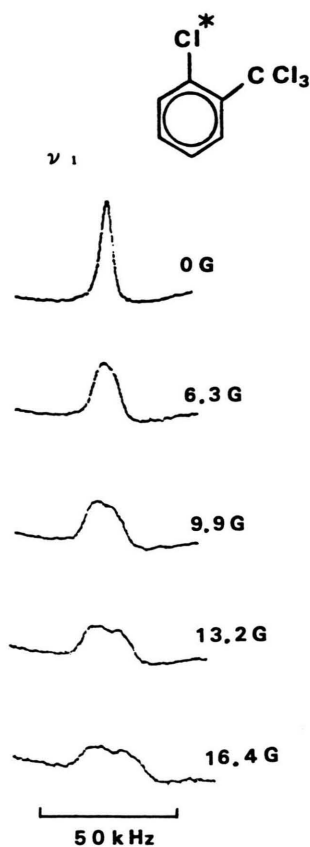


Fig. 14. PZNQR absorption curves at ν_1 for 1-chloro-2-(trichloromethyl)-benzene. An asterisk at a Cl atom in a molecular formula represents a Cl atom responsible for the curve at ν_1 .

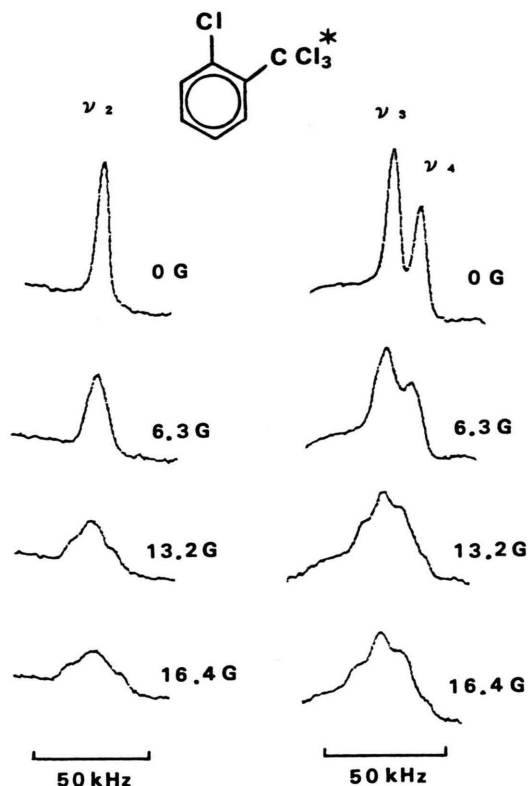


Fig. 15. PZNQR absorption curves at ν_2 , ν_3 , and ν_4 for 1-chloro-2-(trichloromethyl)-benzene. An asterisk at Cl atoms in a molecular formula represents Cl atoms responsible for the PZNQR curves at ν_2 , ν_3 , and ν_4 .

finding that $\eta(\nu_1)$ is somewhat larger than $\eta(\nu_2)$, $\eta(\nu_3)$, and $\eta(\nu_4)$ imply that the double bond character at the Cl atom responsible for $\eta(\nu_1)$ is larger than those for $\eta(\nu_2)$, $\eta(\nu_3)$, and $\eta(\nu_4)$. Consequently, in 1-chloro-2-(trichloromethyl)-benzene, a Cl atom responsible for $\eta(\nu_1)$ seems to attach directly to the benzene ring, while the Cl atoms responsible for $\eta(\nu_2)$, $\eta(\nu_3)$, and $\eta(\nu_4)$ are bound to the C atom of the methyl group. Kiichi *et al.* have studied NQR of 1-chloro-4-(trichloromethyl)-benzene [21] and found η values and resonance frequencies at 77 K: 0.072 and 34.8293 MHz, 0.040 and 38.4404 MHz, 0.023 and 39.2801 MHz, and 0.045 and 39.2801 MHz, respectively. A trend of decreasing η value with increasing resonance frequency is seen for 1-chloro-4-(trichloromethyl)-benzene, as in the case for 1-chloro-2-(trichloromethyl)-benzene.

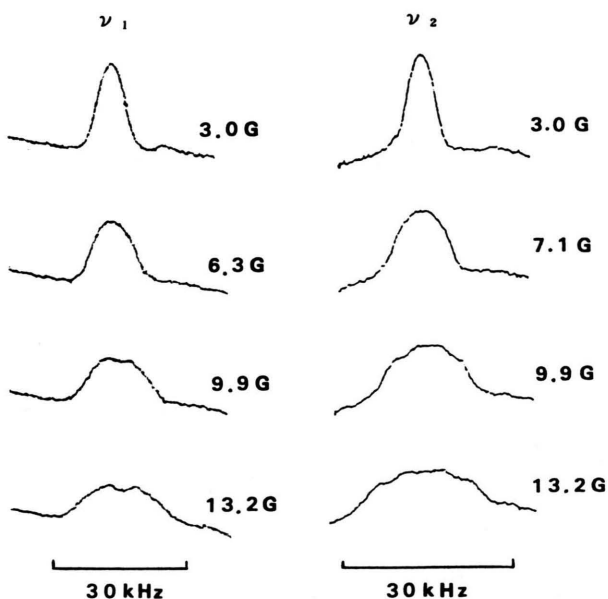


Fig. 16. PZNQR absorption curves at ν_1 and ν_2 for 1,4-dichlorobutane.

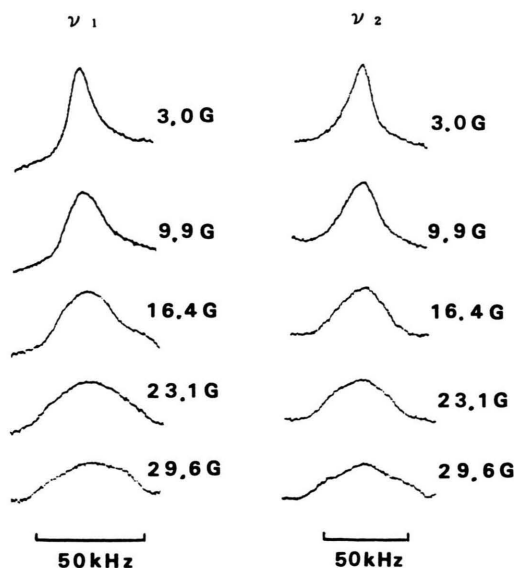


Fig. 17. PZNQR absorption curves at ν_1 and ν_2 for 1,1,1-trichloroethane.

Two absorption lines for 1,4-dichlorobutane were found at 32.619 (ν_1) and 32.878 (ν_2) MHz, indicating that two Cl atoms connected to the terminal C atoms are in inequivalent environments in the 1,4-dichlorobutane crystal. Figure 16 shows PZNQR curves of 1,4-dichlorobutane as functions of magnetic field intensity. Since the curves at ν_1 show the characteristics

Table 2. Resonance frequencies, η values, and coupling constants ($e^2 q Q h^{-1}$) of ^{35}Cl in chlorine compounds at 77 K.

Compound	Frequency (MHz)	η	$e^2 q Q h^{-1}$ (MHz)
Hexachlorobenzene	38.389	small	76.778
	38.464	0.15	76.641
	38.503	0.14	76.756
1-Chloro-2-(trichloromethyl)-benzene	35.796	small	71.592
	39.154	very small	78.308
	39.603	very small	79.206
1,4-Dichlorobutane	39.615	very small	79.230
	32.619	small	65.238
	32.878	very small	65.756
1,1,1-Trichloroethane	37.828	very small	75.656
	38.051	very small	76.102

of type 2, $\eta(\nu_1)$ is evaluated to be very small. On the other hand, the curves at ν_2 are assigned to type 3.

1,1,1-Trichloroethane exhibited two absorption lines at 37.828 (ν_1) and 38.051 (ν_2) MHz. Figure 17 shows PZNQR absorption curves of 1,1,1-trichloroethane. $\eta(\nu_1)$ and $\eta(\nu_2)$ are estimated to be very small on the basis of the simulated pattern of type 3 (shoulder-head-shoulder).

Table 2 summarizes the resonance frequencies, the η values, and the coupling constants for the chlorine compounds examined in this work. The coupling constants in Table 2 were calculated, assuming $\eta = 0$ when it was small or very small.

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