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CHLORINE PURE QUADRUPOLE RESONANCE IN CARBON TETRACHLORIDE EVIDENCE FOR PHASE TRANSITIONS

Shigeo MURATA, Kazuyoshi FUJITA, and Masahiko SUHARA
Department of Chemistry, Faculty of Science, Kanazawa University, Maru-no-uchi, Kanazawa 920

The temperature dependence of ^{35}Cl PQR frequency in CCl_4 has been measured at 77 to 110 K. Three discontinuous behaviors, which are attributable to phase transitions, were found in the temperature regions, 77-90, 90-100, and 90-110 K.

It was first found by Livingston[1] that carbon tetrachloride shows a complex PQR spectrum due to ^{35}Cl nuclei; there being 14 lines at 20 K, and 15 at 77 K. Grechishkin[2] has observed that the spectrum becomes 12 lines pattern at 87 K. Similar change has been reported in the Br PQR spectrum of CBr_4[3]. Gutowsky and McCall[4] have measured the temperature dependence of the resonance frequencies for one of the lines in CCl_4 in the range of 77 to 152 K, and also found that the line was observed to fade out at 155 K considerably below the transition point, 225 K[5-10]. Recently, the temperature variation of the whole resonance pattern has been studied below 77 K by means of a super-regenerative spectrometer by Okuma, Nakamura, and Chihara[11], and they reported that, as suggested by Livingston, 16 lines with almost the same temperature coefficient were observed. In a present work, the precise observation of the temperature dependence of the spectral pattern in CCl_4 has been accomplished in the temperature range above 77 K in order to detect 16 lines pattern and to check the correctness of the reported results.

The sample of carbon tetrachloride was purified in usual manner and stored in liquid nitrogen. A regenerative spectrometer of the Kushida-type[12,13] was used. The sample temperature in the present study was maintained with a constancy of $\pm$ 0.5 K for several hours, or of $\pm$1 K for 20 min at worst case.

Carbon tetrachloride at 77 K exhibits a complex pattern of quadrupole transition; there being 15 lines within 350 kHz, as reported by Livingston. As shown in

Fig. 1, the spectrum was detected with very good S/N ratio and resolution. Closely separated doublet lines, whose frequency separation is 2.6 kHz, were easily observed, although Livingston has first obtained with some difficulty. The temperature dependence of the resonance frequency was observed as shown in Fig. 2. The most significant change in the pattern was found in the three temperature regions; 77-90 K, 90-100 K, and 90-110 K, which will be denoted as regions A, B, and C, respectively. These discontinuities in the temperature dependence are considered to be due to phase transitions. None of the resonance lines arising from coexistence of the different phases were observed. In each of the regions the resonance frequency decreases almost linearly with increasing the temperature. The symbol of the resonance lines in each of the phases will be denoted as ν_A^1, ν_A^2, and so on. The order is defined successively from the line with the highest frequency at the temperature where the maximum multiplet is seen.

Region A --- The 15 lines-pattern containing the closely separated doublet lines at 77 K was found. The lines, ν_A^1 and ν_A^2, coalesce at 84 K and again split into a doublet at higher temperature. Similar behavior can be seen for the lines, ν_A^{10} and ν_A^{11}. The closely separated doublet lines, ν_A^7 and ν_A^8, were detected as a single line above 80 K. All the lines have a temperature coefficient of the same order of magnitude; the average value being -11.8 kHz/K. It was seen that a 12 lines-pattern, as observed by Grechishkin at 87 K, resulted from the temperature gradient at the sample. The 16 lines-pattern, as predicted by Livingston, was not observed at any temperature in this region. Taking into account the reported result[11], one of the lines may be a coalescence of two lines.

Region B --- It should be noted that the 16 lines-pattern was clearly observed at 97-100 K, although the 14 lines-pattern was seen at 90 K. The lines, ν_B^2 and ν_B^3, coalesced at 90 K split into two at 100 K. In contrast, the separated lines, ν_B^5 and ν_B^6, coalesce at 100 K. Closely separated triplet lines, ν_B^{12}, ν_B^{13}, and ν_B^{14}, show the same temperature dependence. The average temperature coefficient of the 16 lines is -12.0 kHz/K.

Region C --- The smaller temperature coefficient compared with those in the above two regions was found; the average coefficient being -6.2 kHz/K. The 15 lines -pattern was seen at 92-102 K, and the 14 lines-one at 106-110 K. The lines, ν_C^2 and ν_C^3, coalesce below 102 K. Contrary to this, the lines, ν_C^9 and ν_C^{10}, as well as the lines, ν_C^{13} and ν_C^{14}, coalesce above 107 K. These facts give the result that there are 16 lines in the whole temperature region C, as in the region B.

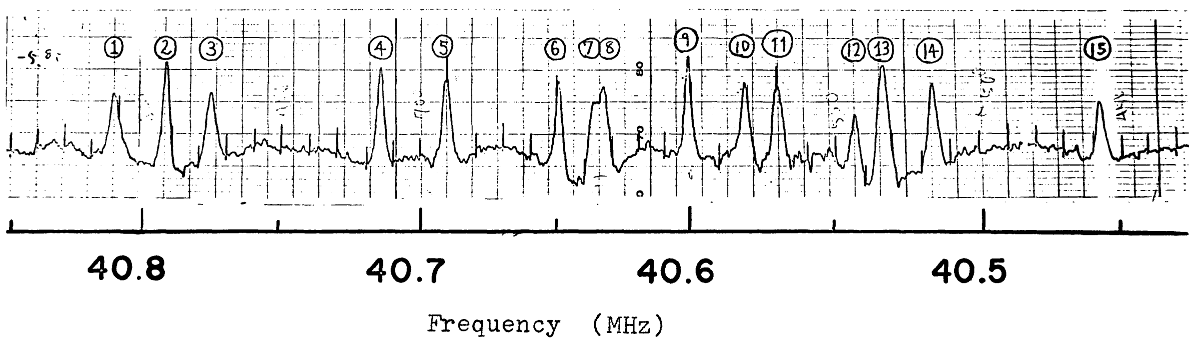

Fig. 1. PQR spectrum of ^{35}Cl in CCl_4 at 77 K by Zeeman modulation

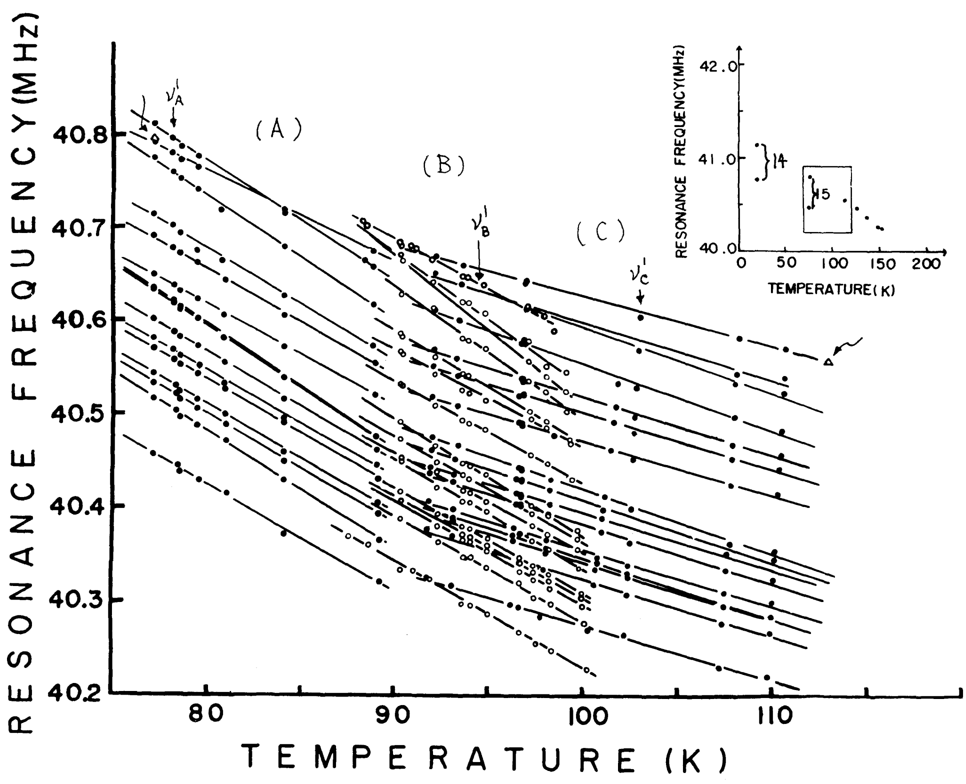

Fig. 2. Temperature dependence of the resonance frequency of the lines in each of the regions, A, B, and C, together with the previous data shown by the symbol △ pointed by arrow (Gutowsky and McCall) and by the symbol • in the insert (Gutowsky and McCall, and Livingston).

The present results show that Gutowsky and McCall's analysis does not give the correct result, because of their failure of finding the phase transitions owing to the large temperature interval being taken. By using the Bayer's theory[14], the average values of the rotational vibration frequency of CCl_4 molecule in crystal were obtained to be 40, 40, and 55 cm^{-1} in the phases, A, B, and C, respectively. These values can be compared with the reported value of 40 cm^{-1}, obtained from the PQR[11] and the specific heat[15] measurements below 77 K.

The remarkable features of the PQR spectra in CCl_4 from 77 to 110 K are pointed out as follows; (1) Similar multiplet pattern with nearly the same number of lines is obtained in the three phases. (2) Discontinuous change of the resonance frequency is not large. and (3) Differences among the temperature coefficients for each of the lines are small. From these facts, it is suggested that the phase transitions obtained are due to a slight change of the crystal structure.

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