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The Chlorine Quadrupole Resonances of Ethane Derivatives

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The temperature broadening of the chlorine quadrupole resonance line-width was studied in three ethane derivatives (1, 1, 1-trichloroethane, hexachloroethane and 1, 1, 1, 2-tetrachloro-2, 2-dimethylethane) below the plastic crystalline phases. Most of the resonance frequencies observed at the temperature of liquid nitrogen were equal to those reported in the literature. The energies of activation (2.2, 2.6 and 4 kcal./mol. respectively for the three compounds mentioned above) were obtained from the line-width versus temperature curves in the low temperature phases. It was suggested, considering the smallness of the energies of activation, that the vibrational rotation of the molecule as a whole rather than the internal axial rotation may exist in those phases.

Gutowsky and McCall(1) and Tatsuzaki and Yokogawa(2) reported a temperature shift of the chlorine quadrupole resonance frequencies in chlorine-substituted hydrocarbons. Many of these compounds possess plastic crystal phases just below the melting points, and the molecules are in rotational or disordered states in such phases. These authors showed, from an analysis of the temperature shift of the resonance frequencies, that the resonance signals of these compounds fades out at certain temperatures below the plastic crystal phases; they interpreted this phenomenon as resulting from the increase in the degree of molecular rotation. The purpose of the present investigation is to study this phenomenon in further detail with respect to the temperature effect of the line-width and of the

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1) H. S. Gutowsky and D. W. McCall, *J. Chem. Phys.*, **32**, 548 (1960).

2) I. Tatsuzaki and Y. Yokogawa, *J. Phys. Soc. Japan*, **12**, 802 (1957).

TABLE I. SUMMARY OF RESULTS OF THE PRESENT EXPERIMENTAL STUDIES

	CH_3CCl_3	C_2Cl_6	$CCl_3CCl(CH_3)_2$
Melting point, °K	240	—	452
Transition point, °K	224 205	344 318	234
Resonance frequency at 77°K, kc.	38216(a) 38036(b) 37820(c)	40752(a) 40710(b) 40678(c) 40539(d)	39159(a) 39092(b) 35192(c)
Fade-out temperature, °K	150	250	230
Activation energy, kcal./mol.	2.2	2.6	4.0

signal-to-noise ratio of chlorine quadrupole resonance signals for 1, 1, 1-trichloroethane, hexachloroethane and 1, 1, 1, 2-tetrachloro-2, 2-dimethylethane at atmospheric pressure.

Experiments

Materials.—Hexachloroethane and 1, 1, 1-trichloroethane of a commericial reagent grade were vacuum-sublimed into glass ampoules for the resonance measurement. The observed melting and transition points are summerized in Table I; they are in satisfactory agreement with those reported in the literature. 1, 1, 1, 2-Tetrachloro-2, 2-dimethylethane was synthesized from chloretone and phosphorus pentachloride by the method reported by McElvin and Stevens.[3] The raw material thus obtained was recrystallized several times from an ethanol solution and sublimed under vacuum into glass ampoules for the measurement. The same material was used for the dielectric measurement. The observed melting and transition points are listed in Table I. The chlorine content of the material purified in this way was analyzed to be 71.74%, almost equal to the calculated values of 72.4%. The electric capacity versus the temperature curve changed quite sharply at the transition point, as is shown in Fig. 1, indicating that the material was quite pure. The plastic crystal phase of this material was observed to be isotropic by optical measurements, and the X-ray diffraction lines of a powder sample of this phase were interpreted satisfactorily as having a body-centered cubic structure.

Chlorine Quadrupole Resonance Measurements.—A self-quenching super-regenerative detector described by Dean[4] was used for the detection of the resonance signals. When the signal was strong, the resonance frequency was measured by an oscilloscope with a heterodyne-frequency meter calibrated by JJY, with an accuracy of ±1 k c. p. s. In order to determine the resonance characteristics, the resonance signal was frequency-modulated with the modulation frequency of 80 c. p. s. amplified with a narrow-band amplifier of the feed-back type, with a band-width of 2 c. p. s. and 80 db. amplification, and then recorded through a phase-sensitive detector. In this case, the accuracy of the frequency measurement was about ±2 k c. p. s.

Measurements at Low Temperatures.—The samples were kept in a petroleum ether bath cooled with liquid nitrogen from outside of the container bath. Below the solidifying temperature of petroleum ether, approximately 120°K, powder of the sodium chloride was mixed with petroleum ether in order to increase the thermal conductivity of solid ether; the temperature was kept very nearly constant, within ±0.1°C/min., during the measurements. Since these substances have marked phase transitions, they have to be cooled very slowly through the transition point in order to make the resonance characteristics reproducible under thermal equilibrium conditions. In the present case, about three hours were required to cool the sample from room temperature to stable and reproducible resonance conditons at the temperature of liquid nitrogen.

Dielectric Measurements.—The dielectric measurements of 1, 1, 1, 2-tetrachloro-2, 2-dimethylethane were carried out using a low-frequency bridge described elsewhere.[5] Since this material decomposes quite easily near the melting point, the measurement was undertaken only below room tempareture with a powder sample kept in a vacuum-sealed glass cell and with a platinum electrode installed inside the cell. By this apparatus, the absolute value of the dielectric constant could not be obtained, but a relative change in the electric capacity of the sample cell with the variation in temperature was measured, as shown in Fig. 1.

Experimental Results and Discussion

1, 1, 1-Trichloroethane.—Three resonance lines a, b and c were observed at the temperature of liquid nitrogen, as Table I shows, in an intensity ratio of roughly 2 : 3 : 1. The a and b lines were identified with those already reported by Gutowsky and McCall.[1] The curves of the temperature versus frequency, the half-value width and the signal-to-noise ratio for the b line are illustrated in Figs. 2, 3 and 4 respectively. The a and c lines have characteristics similar to those of the b line. The contribution of the intramolecular or overall rotational motions of the molecule to the line-width, $\Delta\nu$, of the signal becomes important as the temperature approaches the rotational phase transition point, as is shown by the broken line in Fig. 3 (from 110°K to 170°K). As has been discussed by Das and Hahn,[6] the activation energy, E, for

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[3] S. M. McElvin and C. Stevens, *J. Am. Chem. Soc.*, **69**, 2667 (1947).

[4] C. Dean, *Phys. Rev.*, **96**, 1053 (1954).

[5] S. Kondo and T. Oda, This Bulletine, **27**, 567 (1954).

[6] T. P. Das and E. L. Hahn, " Nuclear Quadrupole Resonance Spectroscopy," Academic Press, New York (1958) PP. 64—70.

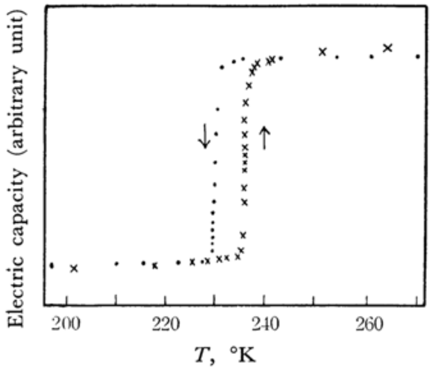

Fig. 1. Electric capacity versus temperature curve of $Cl_3CCl(CH_3)_2$.

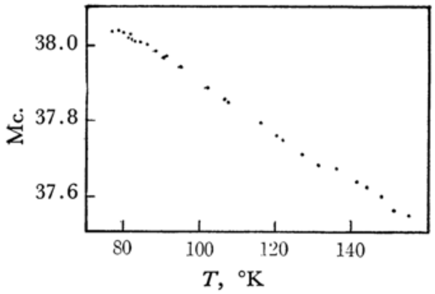

Fig. 2. Frequency versus temperature curve of the b line of Cl_3CCH_3.

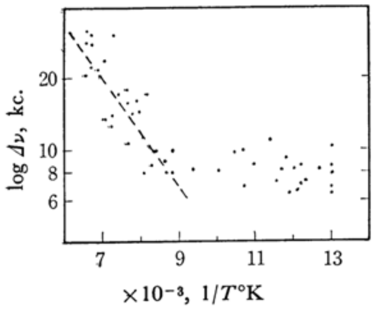

Fig. 3. Half-value width versus temperature curve of the b line of Cl_3CCH_3.

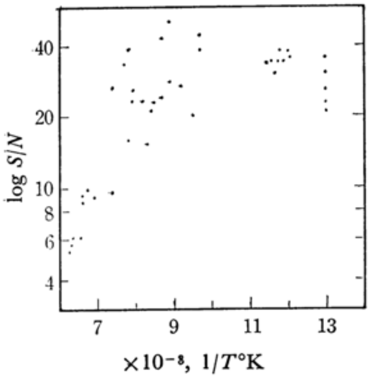

Fig. 4. Signal-to-noise ratio versus temperature curve of the b line of Cl_3CCH_3.

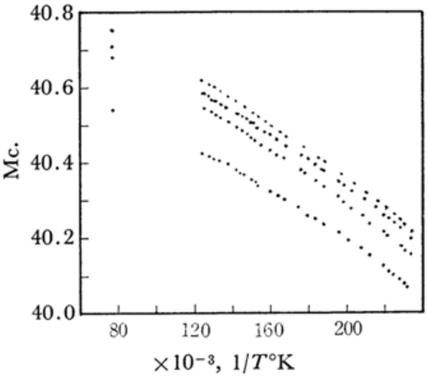

Fig. 5. Frequency versus temperature curves of four lines of C_2Cl_6.

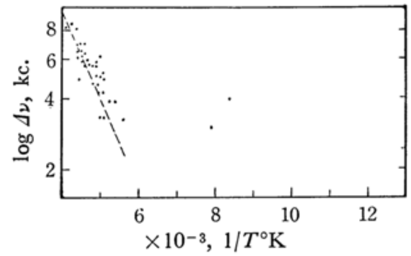

Fig. 6. Half-value width versus temperature curve of the a line of C_2Cl_6.

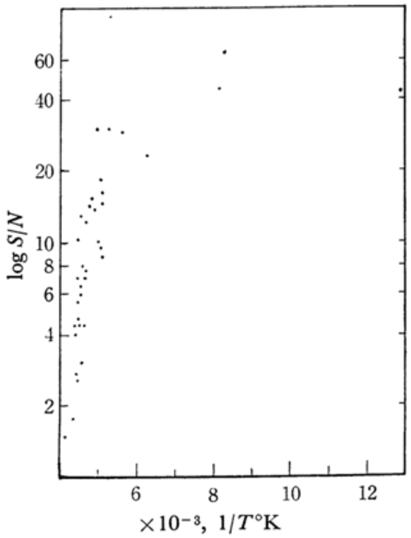

Fig. 7. Signal-to-noise ratio versus temperature curve of the a line of C_2Cl_6.

the molecular rotation can be obtained from the slope of the curve shown in Fig. 3. For example, Buyl-Bodin[7] described this curve by the following expression;

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[7] M. Buyl-Bodin, *Ann. Phys.*, (12) **10**, 533 (1955).

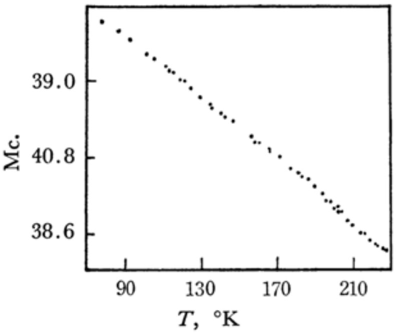

Fig. 8. Frequency versus temperature curve of the a line of $CCl_3CCl(CH_3)_2$.

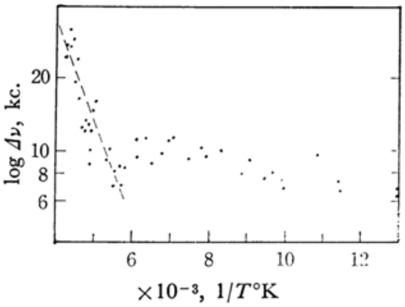

Fig. 9. Half-value width versus temperature curve of the a line of $CCl_3CCl(CH_3)_2$.

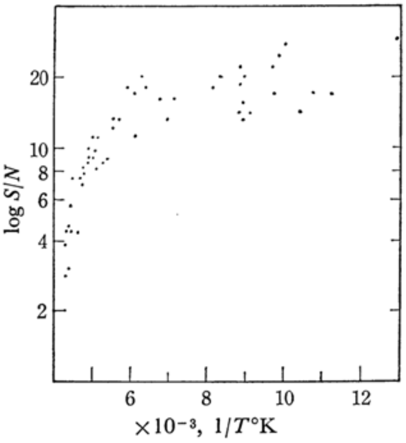

Fig. 10. Signal-to-noise ratio versus temperature curve of the a line of $CCl_3CCl(CH_3)_2$.

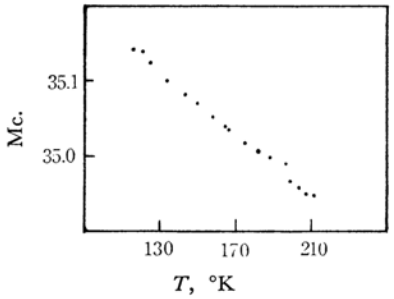

Fig. 11. Frequency versus temperature curve of the c line of $CCl_3CCl(CH_3)_2$.

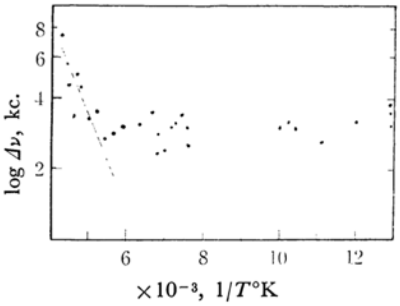

Fig. 12. Half-value width versus temperature curve of the c line of $CCl_3CCl(CH_3)_2$.

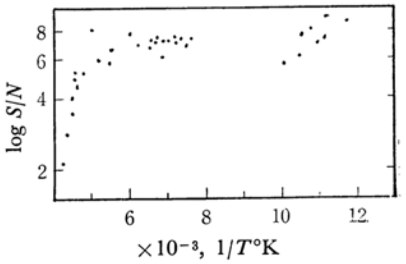

Fig. 13. Signal-to-noise ratio versus temperature curve of the c line of $CCl_3CCl(CH_3)_2$.

$$\frac{1}{\Delta\nu}\frac{\mathrm{d}\Delta\nu}{\mathrm{d}T}=\frac{E}{\boldsymbol{R}T^2}$$

where T is the absolute temperature and $\boldsymbol{R}$ is the gas constant. From this equation, the value of E is calculated to be 2.2 kcal./mol. in the temperature range from 110°K to 170°K. Since the methyl groups of this molecule start rotating at about −180°C, according to the study of nuclear magnetic resonance by Powles and Gutowsky,⁽⁸⁾ it seems that the internal rotation of the constituent groups and the rotatation of the molecule as a whole occur simultaneously near the fade-out temperature.

Hexachloroethane.—The four resonance lines, a, b, c and d, observed at 77°K, can clearly be identified with those reported by Gutowsky and McCall⁽¹⁾ and by Tatsuzaki and Yokogawa⁽²⁾. The curves of the frequency, the line-width and the signal-to-noise ratio versus the temperature for the a line are shown in Figs. 5, 6 and 7 respectively. The corresponding curves of the other lines are similar to those of the a line. The activation energy for rotation, obtained in the same way as in the case of 1, 1, 1-trichloroethane from Fig. 6, (in the temperature range from 160°K to 250°K), is about 2.6 kcal./mol. This value seems to correspond

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8) J. P. Powles and H. S. Gutowsky, *J. Chem. Phys.*, **21**, 1695 (1953).

9) R. Livingston, *J. Phys. Chem.*, **57**, 496 (1957).

to the activation energy of the rotation of the molecule as a whole, since the value is much smaller than the activation energy of the internal rotation of this molecule (about 10 kcal./mol.) obtained by Morino and Iwasaki.[10]

1, 1, 1, 2-Tetrachloro-2, 2-dimethylethane.—Three resonance lines a, b and c were observed as shown in Table I. The a and b lines have frequencies higher than that of the c line. As has been discussed by Hooper and Bray,[11] the a and b lines can be assigned to the three chlorine atoms bonded (more covalently) to the same carbon atom at the position 1 while the c line can be assigned to the single carbon atom bonded (less covalently) to carbon 2.

The curves of the frequency, the line-width and the signal-to-noise ratio versus the temperature for the a and c lines are shown in Figs. 8 through 13. These three lines fade out at about 230°K; this is just below the phase transition temperature (234°K) obtained by the dielectric measurements illustrated in Fig. 1. The activation energies obtained from the line-width versus the temperature curves of the lines a and c shown in Figs. 9 and 12 are about 4 kcal./mol. Figures 9, 10, 12 and 13 indicate that the activation energy and the temperature dependence of the line-width and the signal-to-noise ratio are quite similar in the lines a and c; this may imply that the motions of the chlorine atoms at the positions 1 and 2 are nearly alike as far as the present measurements are concerned. This result may provide further indirect support for the assumption that the molecule as a whole rotates in this temperature range.

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[10] Y. Morino and M. Iwasaki, *J. Chem. Phys.*, **17**, 216 (1949).

[11] H. O. Hooper and P. J. Bray, ibid., **33**, 334 (1960).