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Chlorine Nuclear Quadrupole Resonance Study of the Molecular and the Ionic Crystals of Phosphorus Pentachloride and the Phase Transitions in and between the Two Crystalline Modifications

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The ^{35}Cl quadrupole resonance (NQR) spectra in both the molecular (PCl_5) and the ionic ($PCl_4^+ \cdot PCl_6^-$) solid modifications were measured and assigned, and their temperature dependences (20 to 250°K) were interpreted by a modified Bayer theory. A phase transition of higher order occurs in the ionic solid at 102.3°K which was also revealed by a preliminary heat capacity measurement: There are seven resonance lines below 102.3°K and four above it. An anisotropy in the librational motion is suggested. The molecular solid modification is metastable and transformation into the ionic solid occurs over a range of temperature. This was observed both in the quadrupole resonance spectrum and in the differential thermal analysis; the latter was used to derive the apparent activation energy for the disproportionation reaction. A phase transition occurs also in the molecular solid at 183°K. The partial ionic character of the P-Cl bonds in the two modifications was estimated from the NQR results and could account for the observed chemical shift in the nuclear magnetic resonance of ^{31}P. The ^{35}Cl resonance frequencies in a family of compounds PX_n were correlated.

Phosphorus(V) chlorofluorides, PCl_nF_{5-n}, exist in two different modifications; one is the stable ionic compound and the other is the metastable one which can exist only at low temperatures.[1] A series of interesting experimental studies were recently made by Holmes and other investigators on the molecular structures of these substances.[2-5]

Phosphorus pentachloride is at the extreme of this family of compounds: Its trigonal bipyramidal molecule exists in the gaseous and liquid states,[6-8] whereas its stable modification in the solid state is tetragonal (C_{4h}^4) and the crystal is composed of the two distinct ionic species, PCl_4^+ and PCl_6^-.[9] Recently it was found by infrared spectroscopic study[7] that a metastable modification composed of the molecular unit, PCl_5 can also exist under certain circumstances.

Phosphorus pentachloride may be regarded as a key substance for the systematic, both experimental and theoretical, investigations on the structure, stability, and other properties of phosphorus pentahalides as well as other tri- and pentahalides of the group V elements.

The present paper describes some results of the study of the ionic and molecular modifications of phosphorus pentachloride by nuclear quadrupole resonance (NQR), in an attempt to obtain an insight into the nature of the P-Cl bonds in either solid and the mechanism of the transition between the two solid forms. Preliminary heat capacity results of the ionic solid between 15 and 140°K will also be presented.

Theoretical

Since the general features of NQR are well known,[10,11] it will suffice to discuss here only briefly the relevant points of the theory. In the case of ^{35}Cl or ^{37}Cl, the spin number is 3/2 and the nuclear quadrupole resonance frequency is given by

1) D. S. Payne, *Quart. Revs*, **15**, 173 (1961); S. B. Hartley, W. S. Holmes, J. K. Jacques, M. F. Mole and J. C. McCoubrey, *ibid.*, **17**, 204 (1963); R. R. Holmes, *J. Chem. Education*, **40**, 125 (1963); and the references therein.

2) R. R. Holmes and R. P. Callagher, *Inorg. Chem.*, **2**, 433 (1963).

3) J. E. Griffiths, R. P. Carter, Jr., and R. R. Holmes, *J. Chem. Phys.*, **41**, 863 (1964).

4) R. R. Holmes, R. P. Carter, Jr., and G. E. Peterson *Inorg. Chem.*, **3**, 1748 (1964).

5) R. R. Holmes and R. P. Carter, Jr., *J. Chem. Phys.*, **43**, 1645, 1650 (1965).

6) M. Rouault, *Ann. Phys.*, **14**, 78 (1940).

7) G. L. Carlson, *Spectrochim. Acta*, **19**, 1291 (1963).

8) M. J. Taylor and L. A. Woodward, *J. Chem. Soc.*, **1963**, 4670.

9) D. Clark, H. M. Powell and A. F. Wells, *ibid.*, **1942**, 642.

10) T. P. Das and E. L. Hahn, "Nuclear Quadrupole Resonance Spectroscopy," Academic Press, New York (1958).

11) C. T. O'Konski, "Nuclear Quadrupole Resonance Spectroscopy," in: "Determination of Organic Structure by Physical Methods," Vol. 2, Academic Press, New York (1962).

$$\nu_{2/3\rightleftarrows 1/2}=(eQq/2\boldsymbol{h})\cdot(1+\eta^2/3)^{1/2}, \quad (1)$$

where eQq is the nuclear quadrupole coupling constant and η the asymmetry parameter. In the case of axially symmetric field gradient, $\eta=0$. In a later section of this paper, it will be assumed that P-Cl bonds have nearly axial symmetry, *i. e.* $\eta=0$.

The theory of the temperature dependence of nuclear quadrupole resonance frequency was first developed by Bayer[12] and extended later by Kushida.[13] The resonance frequency at a temperature, $\nu(T)$, is given by

$$\nu(T)=\nu_Q\left\{1-(3\boldsymbol{h}/8\pi^2)\sum_i(1/I_i\nu_i)\cdot\left(1/2+\frac{1}{\exp(\boldsymbol{h}\nu_i/\boldsymbol{k}T)-1}\right)\right\}, \quad (2)$$

$$\nu(0)=\nu_Q\{1-(3\boldsymbol{h}/16\pi^2)\sum_i(1/I_i\nu_i)\},$$

where ν_Q is the resonance frequency for the perfectly static lattice, $\nu(0)$ the resonance frequency at 0°K, ν_j the librational (torsional) or the intramolecular vibrational frequencies of the molecular or ionic units and I_i the corresponding moment of inertia. The summation is taken over all vibrational modes.

The temperature coefficient of the resonance frequency $(d\nu/dT)/\nu$ may easily be derived from Eq. (2);

$$1/\nu\cdot(d\nu/dT)=-(3\boldsymbol{h}^2/8\pi^2\boldsymbol{k}T^2)\sum_i(1/I_i)\cdot\frac{\exp(\boldsymbol{h}\nu_i/\boldsymbol{k}T)}{\{\exp(\boldsymbol{h}\nu_i/\boldsymbol{k}T)-1\}^2}. \quad (3)$$

The informations on the molecular motions in a crystal can be obtained from these equations by measuring the resonance frequencies $\nu(T)$ over a wide temperature range.

The electric field gradient q at a resonant nucleus is related to the ionicity, I, the s- and d-hybridization, s^2 and d^2, and the double bond character π of the chemical bond in which the nucleus participates,

$$eQq=(1-s^2+d^2-I-\pi)\cdot eQq_{at}, \quad (4)$$

according to the Townes-Dailey's theory, where q is the field gradient observed for the molecule and q_{at} is the field gradient in a free atom.[10,14]

Experimental

Phosphorus pentachloride (C.P., Wakō Pure Chem. Ind., Ltd.) was purified by vacuum sublimation under 10^{-3} mmHg, and stored in the NQR specimen cell of 15 mm in outside diameter. The sample coil was set in a Cu-shield and connected to the spectrometer through, in part, a coaxial cable made of cupronickel tube (2 mm i. d.) and a thin stainless steel tube (10 mm o. d.), for the purpose of decreasing the heat conduction, and in part a commercial coaxial cable. The spectrometer is a frequency-modulated super-regenerative type described by Dean.[15] The frequency range from 15 to 35 Mc/sec was scanned for the resonance signals of ^{35}Cl, and the resonance frequencies were measured directly on a CRO combined with an RF-signal generator and an electronic counter (Ono Sokuki Seisakusho, Model Q-181).

The molecular solid PCl_5 was prepared by vacuum sublimation onto a cold wall (below −100°C) of the specimen cell.[7] The temperatures were measured by a Chromel-P-constantan thermocouple calibrated against a platinum resistance thermometer (Leeds & Northrup Co.). The error in the temperature measurement was within 0.1°C.

The heat capacity measurement[16] of the ionic solid and the differential thermal analysis of the molecular solid was also made to examine the thermal properties of these substances. The heat capacity measurement is only preliminary and its details will appear elsewhere.

To assist in the assignment of a number of resonance lines in the ionic crystal, a preliminary NQR measurement was also made on the so-called ionic crystal, $PCl_4^+\cdot SbCl_6^-$. The sample of this crystal was prepared by heating directly the stoichiometric mixture of phosphorus pentachloride and antimony pentachloride.[1]

Results and Discussion

The resonance frequencies in the ionic and the molecular phosphorus pentachloride and also the

Table 1. Resonance frequencies of ^{35}Cl in $PCl_4^+\cdot PCl_6^-$, PCl_5 and $PCl_4^+\cdot SbCl_6^-$ observed at liquid nitrogen temperature

Substance	Species	Resonance line	Frequency Mc/sec
$PCl_4^+\cdot PCl_6^-$	PCl_6^-	ν_1	28.424±0.003
		ν_2	29.720±0.002
		ν_3	30.478±0.006
	PCl_4^+	ν_4	32.288±0.002
		ν_5	32.396±0.002
		ν_6	32.620±0.002
PCl_5	axial	ν_1	29.242±0.003
		ν_2	29.274±0.003
	equatorial	ν_3	33.751±0.002
$PCl_4^+\cdot SbC_6^-$	$SbCl_6^-$	ν_1	24.03 ±0.02
		ν_2	24.96 ±0.02
	PCl_4^+	ν_4'	25.60 ±0.01[a]
		ν_3	32.275±0.003
		ν_4	32.478±0.003

a) This line was assigned to be the ^{37}Cl resonance signal.

12) H. Bayer, *Z. Phys.*, **130**, 227 (1951).
13) T. Kushida, *J. Sci. Hiroshima Univ.*, **A19**, 327 (1955); T. Kushida, G. B. Benedek and N. Bloembergen, *Phys. Rev.*, **104**, 1364 (1956).
14) C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **17**, 782 (1949); **20**, 35 (1952); B. P. Dailey and C. H. Townes, *ibid.*, **23**, 118 (1955).
15) C. Dean and M. Pollak, *Rev. Sci. Instr.*, **29**, 630 (1958).
16) See T. Shinoda, H. Chihara and S. Seki, *J. Phys. Soc. Japan*, **19**, 1637 (1964) for the calorimeter.

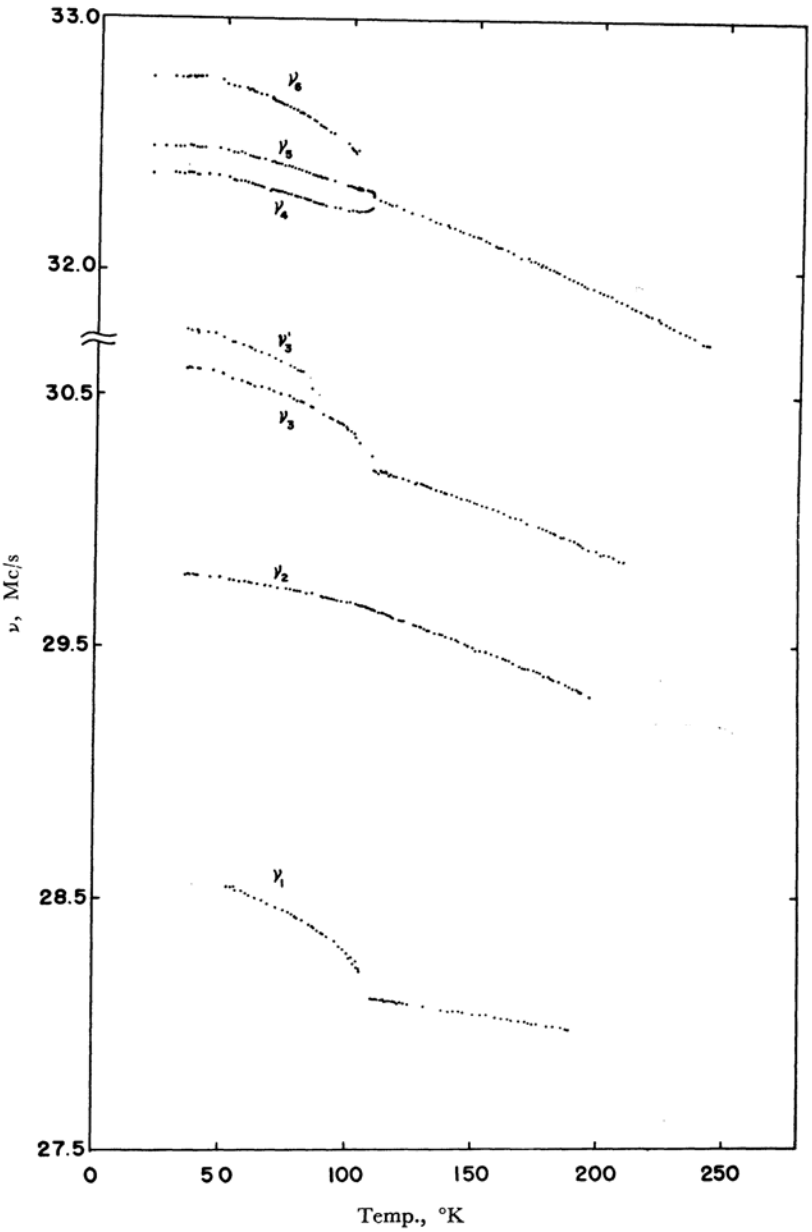

Fig. 1. Temperature dependence of the resonance frequencies of ^{35}Cl in the ionic solid, $PCl_4^+ \cdot PCl_6^-$.

complex compound $PCl_4^+ \cdot SbCl_6^-$ observed at liquid nitrogen temperature are listed in Table 1.

Ionic Solid, $PCl_4^+ \cdot PCl_6^-$. *General Features of the Spectrum.* McCall and Gutowsky[17] reported three resonance lines at 32.282, 32.384, and 32.63 Mc/sec for solid phosphorus pentachloride at −196°C. The spectrum we obtained consists of six lines; three of them at high frequencies apparently correspond to those reported by Gutowsky,[17] *et al.* The three resonance lines at the higher frequencies can be assigned to ^{35}Cl in PCl_4^+, and the three at the lower frequencies to ^{35}Cl in PCl_6^- considering the formal charges on these ions and the P-Cl distances which are shorter in PCl_4^+ (1.98 Å) than in PCl_6^- (2.05 and 2.08 Å).[9]

This assignment is substantiated by a measurement on the complex compound $PCl_4^+ \cdot SbCl_6^-$, in which case two lines due to ^{35}Cl were observed at around 32 Mc/sec and two additional lines around 24 Mc/sec. The former two lines lie

17) D. W. McCall and H. S. Gutowsky, *J. Chem. Phys.*, **21**, 1300 (1953).

near the three in the high frequency region in the ionic phosphorus pentachloride, whereas the latter two lie much lower than any line in the ionic phosphorus pentachloride. As the inter-ionic contribution to the field gradient is usually very small, it is reasonable to assign the lines at 32 Mc/sec to ^{35}Cl in PCl_4^+ in both $PCl_4^+ \cdot PCl_6^-$ and $PCl_4^+ \cdot SbCl_6^-$.

Figure 1 shows the temperature dependence of ^{35}Cl NQR frequencies of the ionic phosphorus pentachloride from 30°K to above 200°K. A line denoted by ν_3', which was observed at low temperatures and faded out at about 80°K, was confirmed not to be a side band of ν_3. As the temperature was increased, distinct changes were observed in the resonance frequencies between 100 and 110°K, where the upper three lines coalesced to a single line and also two other lines except ν_2 displaced considerably to the lower frequency side. The number of resonance lines is in agreement with that expected from the crystal structure determined at room temperature. All lines gradually broadened on further heating and finally faded out above 200°K. The behavior at around 110°K is characteristic of a higher order phase transition as is usually observed by NQR.[18] The fade-out phenomena are also common in NQR and can be due to highly excited motion of molecules or ions, reorientational and other,[19] and/or to thermal creation of lattice imperfections.

In correspondence to the anomaly observed around 110°K by NQR, the heat capacity of the ionic solid, shown in Fig. 2, indicates the presence of a small λ-type anomaly with a peak at 102.3°K. Since the small size of the calorimeter employed limited the accuracy attainable, a more accurate determination of the heat capacity is being undertaken and will be reported elsewhere.

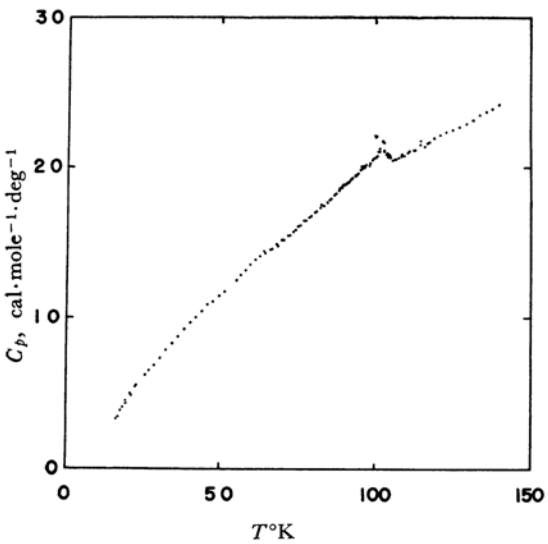

Fig. 2. Heat capacity of the ionic solid, $PCl_4^+ \cdot PCl_6^-$.

Librational Motions. From the results of the NQR measurements, the libration frequencies of PCl_4^+ and PCl_6^- ions were calculated by using Eq. (2), where the intra-ionic contributions were evaluated with the help of infrared and Raman data,[20] $\nu(0)$'s were obtained by a smooth extrapolation of the resonance frequencies to 0°K, and the moments of inertia $I_l(PCl_4^+)=618\cdot10^{-40}$ g·cm^2 and $I_l(PCl_6^-)=987\cdot10^{-40}$ g·cm^2 were obtained from the geometry of the ions.[9] The libration frequencies thus obtained are listed in Table 2.

Table 2. Libration frequencies in the ionic solid, $PCl_4^+ \cdot PCl_6^-$

Species	Moment of inertia 10^{-40}g·cm^2	Temp. °K	Libration frequency cm^{-1}		
PCl_6^-	986	55	45 (ν_1)	66 (ν_2)	51 (ν_3)
		82	36 (ν_1)	58 (ν_5)	41 (ν_3)
PCl_4^+	618	57	75 (ν_4)	66 (ν_5)	55 (ν_6)
		88	57 (ν_4)	56 (ν_5)	44 (ν_6)

Three things are to be noted in this table: a) The apparent librational frequency calculated on the basis of the temperature dependence of a single resonance line is not constant but is shifted to the lower wave number side as the temperature increases. The behavior is not itself surprising because the thermal expansion of the crystal could give rise to a small change in the potential energy of the librating units, which in turn affects the librational frequencies to a greater extent. Alternatively, one can choose a single set of values for ν_l and I_l which give a close fit of Eq. (2) with the experimental temperature dependence of NQR frequencies in a limited range of temperature. However, the values of I_l chosen as such vary from 7 to 45 g·cm^2 depending on which resonance line is referred to in the calculation; these values differ by a factor of 20 or more from those consistent with the known geometry of the ions. The same situation has been encountered by others.[19,21] It may be that the simple theory of the Bayer type fails to apply to complex crystals. This point will be discussed in further detail in a later paper

18) See for reference, G. Boundouris, *J. Phys. radium*, **23**, 43 (1962).
19) H. S. Gutowsky and D. W. McCall, *J. Chem. Phys.*, **32**, 548 (1960).
20) The spectroscopic data was taken from Ref. 7. The line at the lowest wave number, 62 cm^{-1}, was excluded because inclusion of this line makes libration frequency negative.
21) G. A. Jeffrey and T. Sakurai, "Application of Nuclear Quadrupole Resonance," in: "Progress in Solid-State Chemistry," Vol. 1, Pergamon Press, New York (1964).

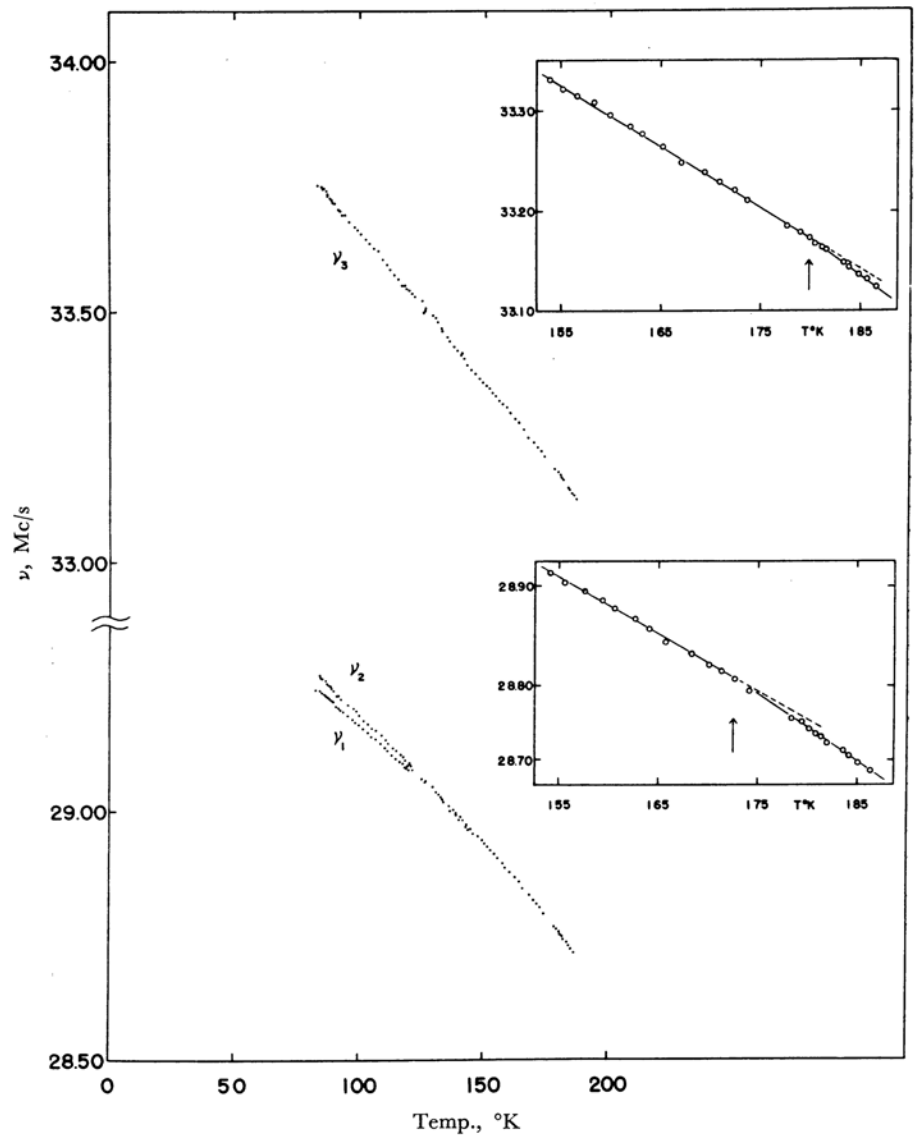

Fig. 3. Temperature dependence of the resonance frequencies of ^{35}Cl in the molecular solid, PCl_5.

on solid chlorine.[22] It seems at the moment more adequate to explain the deviations from Eq. (2) in terms of the temperature dependence of the librational frequency in the *'quasi-harmonic'* approximation.

b) The ν_l values from ν_1, ν_2, and ν_3 takes different values at the same temperature; this may arise from the anisotropy of the librational motions about the three principal axes of the moment of inertia of ions.

c) It seems to be significant to note that ν_l (PCl_4^+) values are generally larger than $\nu_l(PCl_6^-)$ at corresponding temperatures.

Molecular Solid, PCl_5. The NQR lines of the molecular solid PCl_5 were observed at the frequencies given in Table 1, with some difficulty, by direct sublimation into the specimen cell at liquid nitrogen temperature. The resonance frequencies are different from those obtained in the case of the ionic solid. The resonance lines are considerably sharp; this fact suggests that the molecular solid modification, though it is a metastable one, is fairly perfect crystalline phase. Furthermore, its crystal structure may be relatively simple because there were only three resonance lines observed. With reference to the results of the infrared spectral measurements,[8] the electron diffraction study on

22) N. Nakamura and H. Chihara, "Nuclear Quadrupole Resonance of ^{35}Cl and ^{37}Cl in Solid Chlorine," to be published in *J. Phys. Soc. Japan*, **22**, No. 1 (1967).

the gaseous PCl_5,[6] and the NQR measurements on the phosphorus chlorofluorides,[4] the assignment of the resonance lines of PCl_5 was made as follows: The line at 33.75 Mc/sec was assigned to ^{35}Cl lying on the basal plane of the molecular bipyramid (referred to as the equatorial chlorine) and the two others at 29.2 Mc/sec to ^{35}Cl on the molecular three-fold axis (referred to as the axial chlorine).

Figure 3 shows the temperature dependence of the resonance frequencies from the liquid nitrogen temperature to where the lines become invisible. It is interesting to note that the separation between the two lines at 29.2 Mc/sec decreases as the temperature rises and they coalesce into a single line above 120°K. As seen in the inserts of Fig. 3, the resonance frequencies change almost linearly with the temperature, with a small but distinct change in slope in each resonance line around 180°K. This may be related to a phase change in the molecular solid mentioned below but its mechanism is yet to be clarified.

The molecular libration frequencies were computed by using Eq. (3): The intramolecular contributions were calculated as described in the previous section; the moments of inertia relevant in the calculation were obtained with the help of the electron diffraction data on the gaseous PCl_5.*1 [6]

In doing so, the libration frequencies about the two principal axes perpendicular to the molecular three-fold axis was first calculated from ν_1 and ν_2, and that frequency value was then used to obtain the other libration frequency about the three-fold axis from ν_3. Therefore these two librational modes could be completely separated. The result is shown in Table 3. The libration frequencies obtained are almost constant over a wide temperature range, so that the motions can be described with single sets of ν_l's and I_l's in contrast to the case of the ionic solid. It is interesting that $\nu_l = 39\ cm^{-1}$ about the three-fold axis is somewhat larger than $\nu_l = 32\ cm^{-1}$ about the other two axes, which result suggests some anisotropic librational motions.

Table 3. Libration frequencies in the molecular solid, PCl_5

Mode	Moment of inertia $10^{-40}g\cdot cm^2$	Temp. °K	Libration frequency cm^{-1}
Librations about the basal axes	734	100	32 (ν_1) 31 (ν_2)
		150	33 (ν_1)
Libration about the three-fold axis	736	100	39 (ν_3)
		160	39 (ν_3)

*1 The figures adopted here are $734\cdot10^{-40}\ g\cdot cm^2$ (about the three-fold axis) and $736\cdot10^{-40}$ (perpendicular to that axis).

The Disproportionation Reaction, $2PCl_5 \rightarrow PCl_4^+\cdot PCl_6^-$. The quadrupole resonance spectrum of the molecular solid PCl_5 becomes less intense as the temperature is raised, the change beginning gradually at about 110°K, until eventually it fades out near 190°K. On the other hand, the spectrum of the ionic solid begins to appear upon standing overnight near 190°K. This is apparently due to the disproportionation reaction $2PCl_5 \rightarrow PCl_4^+\cdot PCl_6^-$ occurring in the solid phase. This reaction has some consequences in the result of the differential thermal analysis (DTA) shown in Fig. 4; *i. e.* an exothermic effect caused probably by the reaction is seen between 165°K and 214°K. In addition a sharp endothermic effect due probably to a phase transition in the molecular solid is also observed at 183°K.

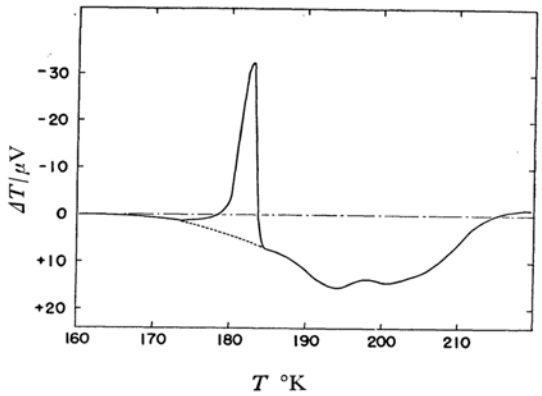

Fig. 4. DTA curve of the molecular solid, PCl_5.

There are two broad maxima in the exothermic part of the DTA curve at 194°K and 201°K. This suggests that the reaction may proceed in two consecutive steps. The DTA curve can be used to estimate the rate constant of the reaction as a function of temperature at least for the first one of the steps by applying Borchardt and Daniels' treatment.[23] In the case of the reaction of the first order, their equation for the rate constant k reads

$$k(T) = \Delta T/(A-a(T)), \qquad (5)$$

where ΔT is the temperature difference between the sample and the reference material, A is the total area under the DTA peak corresponding to the overall heat of reaction and a is the area of the part of the peak which had been swept when the temperature reached T. In evaluating $k(T)$, the endothermic part of the DTA curve was ignored and a smooth dotted curve was drawn as shown in Fig. 4. This type of analysis here extended only between 178 and 192°K and in

23) H. J. Borchardt and F. Daniels, *J. Am. Chem. Soc.*, **79**, 41 (1957).

this temperature region, the $\log k$ plotted against the reciprocal of the absolute temperature shows that the Arrhenius equation

$$k = k_0 \exp(-Q/RT)$$

applies with the numerical value of $k_0 = 4.4 \cdot 10^{13}$ sec^{-1} and $Q = 8.6$ kcal/mol (see Fig. 5). In view of a number of assumptions made in the present treatment, these figures must be taken not literally

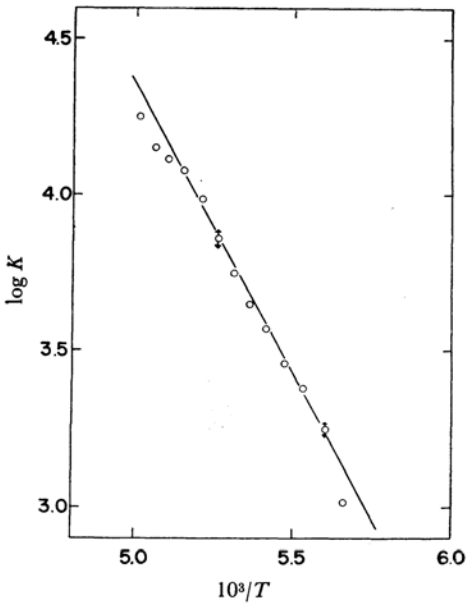

Fig. 5. Rate constant, k, plotted against $1/T$.

but as indicating their orders of magnitude. Yet it is interesting to remark that the reaction is an exothermic one with a relatively small heat of activation and must involve diffusion of chloride ions in the molecular mechanism of the reaction.

We have little clue to the nature of the endothermic transition of the molecular solid at 183°K. It is not evident whether this transition takes place intrinsically or it is catalyzed by the creation of imperfections in the lattice due to the disproportionation reaction. An interesting coincidence, however, was observed that the NQR spectrum of the molecular solid faded out at the temperature where the endotherm of the DTA was concluded. This may suggest that the transition is associated with a high degree of excitation of the molecular motions.*2 Fuller understanding of the processes that occur in the molecular solid awaits the result of its structure determination now being undertaken by Katada and Kakinoki at the Osaka City University by the method of electron diffraction.

The P-Cl Bond Nature. The P-Cl bond distances are given in Table 4 for the three phosphorus polyhedra. The nature of a chemical bond may be characterized by fractional contributions of ionicity, double bond character, s-, p-, d- nature, *etc.* The nuclear quadrupole resonance data alone can not fix all of these fractions unless other informations are incorporated with them. The partial double bond character may be estimated from the bond distance according to the Pauling scheme.[24] If one assumes the s^2 and d^2 in the covalent character to be 15 and 0% respectively in all the Cl bonds as has been done by Townes and Dailey,[14] Eq. (4) can yield an estimate of the partial ionic character of the bonds. Table 4 gives such estimates.

TABLE 4. THE NATURE OF P-Cl BONDS IN PCl_5, PCl_4^+ AND PCl_6^- a)

Species	Bond distance Å	% Double bond character	% p-Bond character	% Ionicity
PCl_5, equatorial	2.01 b)	8	62	15
PCl_5, axial	2.07 b)	0	53	32
PCl_4^+	1.98	18	59	8
PCl_6^-	2.05, 2.08	0	54	31

a) 15% s-character and 0% d-character are assumed for all P-Cl bonds.
b) Gaseous value (Ref. 6).

A third experimental information available is the NMR chemical shift of ^{31}P in PCl_5, PCl_4^+, and PCl_6^-, in which the P atoms possess hybridized orbitals sp^3d, sp^3 and sp^3d^2, respectively. Gutowsky *et al.*[25] showed that the second-order paramagnetic term in the chemical shift is given by

$$\sigma^{(2)} = \sigma_0 \cdot (\langle 1/r^3 \rangle_p P_u + \langle 1/r^3 \rangle_d D_u) \qquad (6)$$

where σ_0 is a constant appropriate to the nucleus under consideration and P_u and D_u are the number of the unbalanced valence electrons in the p and d orbitals. P_u and D_u then determine the average partial ionic character I of the bonds. The differences in the chemical shifts were thus calculated*3 by taking the average I values, $\langle 1/r^3 \rangle_{3p} = 3.4$ at. units, and $\langle 1/r^3 \rangle_{3d} = 0.5$ at. units

*2 It should be pointed out here that the heating rate in the DTA measurement was about 1.2°C/min, very much faster than in the NQR measurements (0.15°C/min, at the fastest) in which the temperature was almost stationary most of the time. Therefore it is possible that in the NQR measurements, the molecular solid had been converted to the ionic solid before it reached the transition point and thus the fade-out of the spectrum was simply due to non-existence of the molecular solid.

24) L. Pauling, "The Nature of the Chemical Bond," Third Ed., Cornell University Press, Ithaca, New York (1960), Chap. 7.
25) C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, **40**, 1714, 2285 (1964).

*3 Values for P_u and D_u were computed for each of the species PCl_4^+, PCl_5, and PCl_6^- by the method of LCAO-MO analogous to the case of xenon fluorides.[25]

and are listed in Table 5. In the same table are also given the experimental values[26,27] and the calculated values for $I=0$ for the sake of comparison. A constant value of σ_0 has been assumed which gives a best fit of $\sigma^{(2)}$ to the experimental data (1600 ppm for finite I's and 870 ppm for $I=0$). Table 5 indicates that some partial ionic characters, as derived from Cl NQR spectra (Table 4), have to be included in order to obtain a good agreement, with experimental results, in the relative magnitudes of chemical shifts. The

Table 5. Difference in ^{31}P chemical shifts (ppm) in PCl_4^+, PCl_5 and PCl_6^- calculated with and without the ionicity listed in Table 4.

	Ionicity included	$I=0$ assumed	Experimental
$\sigma(PCl_5)-\sigma(PCl_6^-)$	−220	−194	−226
$\sigma(PCl_5)-\sigma(PCl_4^+)$	158	194	160
$\sigma(PCl_6^-)-\sigma(PCl_4^+)$	377	387	386

difference in the ionic character between the equatorial and the axial bonds in PCl_5 may be related to the difference in the bond dissociation energies[28] and in turn may play a role in the disproportionation reaction in the solid state.*4 Theoretical treatments of the electronic structures of trigonal bipyramidal molecules have been reported,[29-32] but they are not sufficiently precise to explain the NQR frequencies in these three species.

Correlation of the ^{35}Cl NQR Data on the PX_n Family. Holmes and others have related ^{35}Cl resonance frequencies to the number of chlorine atoms bonded to the central atom in PX_n type compounds in Fig. 4 of Ref. 4. They pointed out that a regularity can be seen between the ^{35}Cl resonance frequency and the number of chlorine atoms forming the equatorial bond in PCl_nF_{5-n}, and that this regularity is opposite to what one might expect on the basis of the electronegativity considerations. It is interesting to add to their figure the results on PCl_4^+, PCl_6^-, PCl_5, and $SbCl_6^-$ obtained in this paper, and $SbCl_5$ on which the nuclear quadrupole resonance frequencies were re-determined.[33] The result is shown in Fig. 6. In this figure, a tendency of the increase in ^{35}Cl resonance frequency with the number of Cl is clearly recognized about the equatorial bond, and the same trend but to a lesser extent is also seen in the axial bond in the series of PCl_nF_{5-n}, which is analogous to the trend seen in the series of CCl_nH_{4-n}.[34] It is rather surprising to see that the average resonance frequency of PCl_4^+

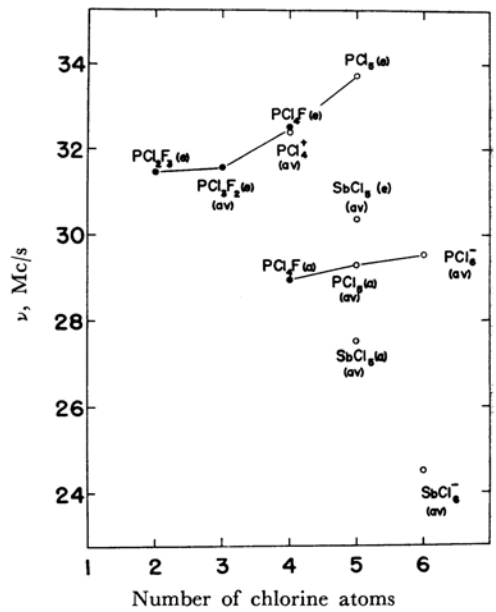

Fig. 6. Resonance frequencies plotted as a function of the number of chlorine atoms bonded to the central atoms, P or Sb. (a) and (e) stand for the axial and the equatorial chlorine sites, respectively, and (av) means averaging over closely spaced resonance frequencies. (Filled circle, after reference 4; open circle, present authors)

falls on the line for the equatorial chlorines and that of PCl_6^- lies on the line for the axial chlorines. This fact suggests that the bond character in PCl_4^+ is similar to that in the equatorial bonds in PCl_5 and the bond in PCl_6^- to the axial bond in PCl_5. Therefore, the orbitals in these three species may not be ideally hydridized ones as have been represented by sp^3, sp^3d, and sp^3d^2, but it may be more reasonable to treat these complex bonds as some combinations of the hydridized orbitals, in which the inductive and the steric effects also play important role.

Conclusion

The ^{35}Cl quadrupole resonance frequencies over the temperature range, 20—250°K, were analyzed

*4 The bond distances in PCl_5 in the solid state may differ significantly from those in the gas phase in such a way that the difference in the ionic character should be amplified, to account for the instability of PCl_5 molecules in the solid as compared in the gas or in solution.

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to yield some information concerning the molecular librational motion and the nature of the P–Cl bonds in solid PCl_5 and $PCl_4^+ \cdot PCl_6^-$. The disproportionation reaction or the transformation from the PCl_5 to the $PCl_4^+ \cdot PCl_6^-$ solids is apparently related to the bond properties in these two species. The nature of the phase transitions in the two solid modifications is yet to be examined and this will be discussed in a later paper when the results of the more accurate heat capacity measurements as well as the X-ray and the electron diffraction studies become available.

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