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# Nuclear Magnetic Resonance Spectra of Crystals Rotated Macroscopically: Fine Structure of the Spectrum of Phosphorus Pentachloride

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*Summary.*

It is pointed out that the dipolar broadening of the nuclear magnetic resonance spectrum of a solid may effectively be removed by rotating the sample at a high speed about an axis inclined with an angle 54° 44′ to the direction of the field. Using this technique the doublet fine structure of the $^{31}P$ spectrum of solid phosphorus pentachloride has been recorded. The two lines are ascribed to the different chemical shifts in the $(PCl_4)^+$ and $(PCl_6)^-$ ions of which the solid is composed. The two shifts relative to aqueous phosphoric acid are found to be + 281 and — 96 p.p.m.

When a solid whose n.m.r. spectrum is determined predominantly by nuclear dipolar interactions is rotated at high speed its spectrum changes. (Andrew, Bradbury and Eades 1958 *a*, *b*, Lowe 1959). It now consists of a central line narrower than the original static line, flanked by satellite lines set at integral multiples of the rotation frequency on either side of the central line. When the rotation rate exceeds the static linewidth, the satellites are resolved from the narrowed central line. As the rotation rate is increased the satellites move out and their intensity is diminished in such a way as to preserve the invariance of the second moment of the whole spectrum. When the rotation rate becomes much greater than the static linewidth the satellites are unobservably weak so that the narrowed central line alone is recorded. A detailed discussion of the form of the spectrum is given in the paper by Clough which follows. The width of the narrowed central line is given in first approximation by the factor $\frac{1}{2}(3\cos^2\gamma - 1)$ times the width of the static line, where $\gamma$ is the angle between the axis of rotation and the direction of the applied magnetic field. We have found that the width of the central line follows this angular dependence quite well (Andrew, Bradbury and Eades 1959). In particular when $\gamma = \cos^{-1} 1/\sqrt{3} = 54^0\,44'$ the central linewidth is found, as predicted, to be quite small. For this orientation of the axis the static dipolar interaction is zero, and at high speeds of rotation the dipolar breadth of the central line should be small as in a liquid.

Fine structure of the type encountered in the high-resolution spectra of liquids is not normally observed in the n.m.r. spectra of solids, since it is masked by the stronger dipolar interactions. However, high-speed rotation of solids at the angle 54° 44′ offers the possibility of removing the dipolar broadening and thus of revealing fine structure.

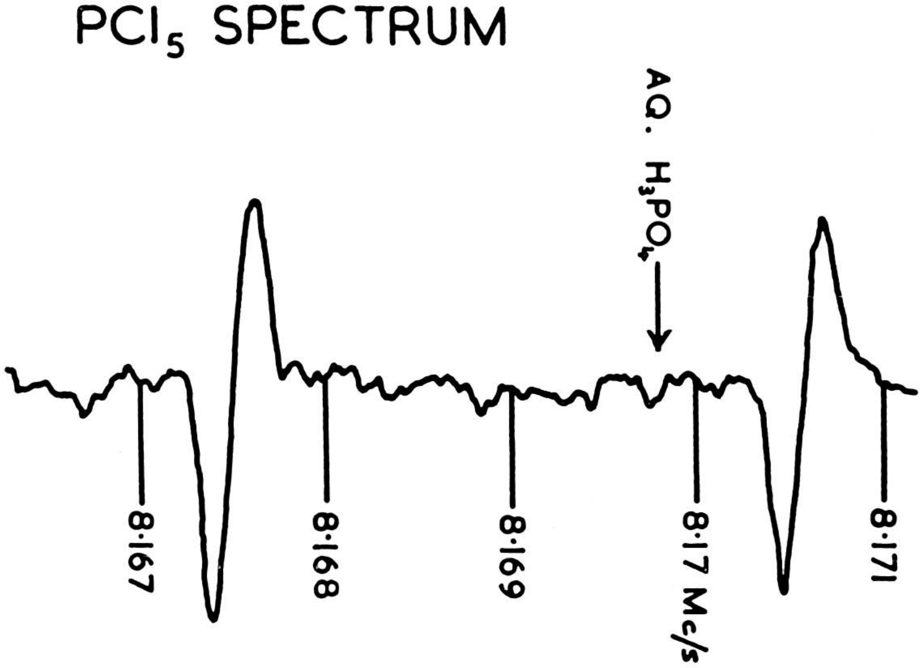

*Figure Caption.* $^{31}P$ magnetic resonance spectrum of polycrystalline phosphorus pentachloride rotated at high speed. The resonance frequency of the reference compound (85% aqueous phosphoric acid) is also indicated; this frequency was determined from recordings taken immediately before and after.

An example of the application of this method is provided by phosphorus pentachloride. The $^{31}P$ resonance spectrum of a polycrystalline sample of phosphorus pentachloride rotated in an airtight container at the angle 54° 44′ is shown in the figure. The sidebands are scarcely distinguishable from the noise background, and the central spectrum consists of two sharp lines of approximately equal intensity. It is known from an X-ray diffraction study by Clark, Powell and Wells (1942) that in the solid state phosphorus pentachloride consists of equal numbers of tetrahedral $(PCI_4)$

and octahedral $(PCI_6)^-$ ions packed in a tetragonal lattice. It is therefore reasonable to identify the two spectral lines with phosphorus nuclei in the two types of ion, the separation between the lines being ascribed to their different chemical shifts. In order to be sure that the separation does in fact have its origin in different chemical shifts measurements are in hand at different field strengths.

The doublet separation corresponds to a difference in chemical shift of 377 ± 10 parts per million. The chemical shifts * of each line have also been measured relative to the usual phosphorus standard, namely aqueous phosphoric acid, and are found to be + 281 and — 96 p.p.m. These shifts fall within the range + 448 to — 222 p.p.m. recorded for various liquid specimens (see for example Pople, Schneider and Bernstein 1959), though the difference between the shifts for the two ions is remarkably large.

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## *Résumé.*

### SPECTRES DE RÉSONANCE MAGNÉTIQUE NUCLÉAIRE DE CRISTAUX TOURNÉS MACROSCOPIQUEMENT;
### STRUCTURE FINE DU SPECTRE DU PENTACHLORURE DE PHOSPHORE

On a montré que l'élargissement dipolaire du spectre de résonance magnétique d'un solide peut être supprimé de façon effective par rotation de l'échantillon à grande vitesse autour d'un axe incliné d'un angle de 54° 44′ sur la direction du champ. En employant cette technique la structure fine du doublet de $P^{31}$ du pentachlorure de phosphore solide a été enregistrée.

Les deux lignes sont dues aux shifts différents des ions $(PCl_4)^+$ et $(PCl_6)^-$ dont est composé le solide. Les deux shifts sont trouvés, vis-à-vis d'une solution aqueuse d'acide phosphorique à + 281 et — 96 p.p.m.

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* The spectra were measured using a fixed field and a variable radiofrequency. The shift is therefore defined as $(\nu_r - \nu_c)/\nu_r$, where $\nu_c$ and $\nu_r$ are the frequencies of the compound and the reference respectively. This is equivalent to the usual definition $(H_c - H_r)/H_r$ when the frequency is held constant and the field is varied.