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Space group identification by proton magnetic resonance. By R. CHIDAMBARAM, *Atomic Energy Establishment, Trombay, Bombay, India*

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The method of identifying the space group of a crystal by studying the systematic absences of certain classes of reflexions in the X-ray diffraction pattern is often ambiguous, owing mainly to the Friedel law, which introduces an artificial centre of symmetry into the pattern. The purpose of this note is to point out that it is often possible to resolve this ambiguity by examining the magnetic resonance pattern of the protons in the crystal.

The resonance pattern for a 2-proton system (like a water molecule) inside a crystal consists of a doublet, and by studying the doublet separation for a sufficiently large number of orientations with respect to the steady magnetic field both the length and the orientation inside the unit cell of the inter-proton vector (hereinafter called the p - p vector) can be determined (Pake, 1948). The complete resonance pattern for any crystal containing 2-proton systems will be a superposition of the doublets from the various non-parallel p - p vectors in the unit cell (the pattern would also contain the lines from the other protons in the unit cell but it is possible to isolate them).

Now, the procedure of using proton magnetic resonance data to identify space groups consists in first calculating the number of non-parallel p - p vectors in the unit cell and their mutual symmetry relationships for the two or more space group choices provided by the X-ray method, and then determining which of them fits the experimental pattern. We will now consider a few examples to show the application of the method:

(a) $P1$ and $P\bar{1}$. Two p - p vectors in the unit cell of a crystal of space group $P1$ would be mutually unrelated and non-parallel while in the space group $P\bar{1}$ they would be related by the centre of symmetry so that there would be only one non-parallel vector.

(b) Cc and $C2/c$. Four p - p vectors in the unit cell of a crystal of space group Cc may be placed in general positions and the resonance pattern will be that due to 2 non-parallel vectors related by mirror symmetry across the (010) plane, whereas in the space group $C2/c$ these vectors have to be placed in special positions lying on twofold axes so that there would be only one non-parallel vector lying in the (010) plane.

The latter example applies to the case of potassium oxalate monohydrate, regarding whose space group there has been some dispute (Jeffrey & Parry, 1954). It was shown by Chidambaram (1961) that the p - p vectors of this crystal lie within $\pm 1^\circ$ of the (010) plane so that the space group is most likely to be $C2/c$. The structure of this crystal has been refined successfully on the basis of this space group both by X-ray diffraction (Ramaseshan, Vaidya & Swaminathan, 1964) and by

neutron diffraction (Chidambaram, Sequeira & Sikka, 1964). Recently, Pedersen & Holcomb (1963) have also examined the proton magnetic resonance of this crystal and assigned it to the space group $C2/c$.

The following points may be noted:

1. Though in principle the method is applicable to resonance patterns obtained from protons in spin systems more complicated than 2-proton systems, unscrambling the experimental curves is difficult and often impossible in these cases. This limits the application of the method to crystals containing H_2O molecules or CH_2 groups. It could probably be extended to crystals containing NH_2 groups if one used double nuclear resonance and washed out the dipolar interaction due to the N nucleus. Between them, however, these groups cover quite a large number of crystals.

2. *Ab initio* it is not possible to proceed from the proton magnetic resonance data. For example, four p - p vectors in a unit cell of a crystal of space group $P2/m$, $P2/c$, $P2_1/m$, $P2_1/c$, Cm , $C2$ or Cc would give the same pattern symmetry. The method has, therefore, to be applied at the stage when the X-ray diffraction data have given the number of formula units in the unit cell and the systematic absences have afforded the space group alternatives. Sometimes the choice may also not be complete. For example, $P2/m$ can be distinguished from Pm and $P2$ but the latter are usually indistinguishable from each other.

3. There is a small but finite probability that the configuration of the p - p vectors may simulate a symmetry (within the accuracy of the experiment) which is higher than what is required by the space group. Such difficulties due to pseudo-symmetry are also sometimes encountered in the statistical methods of analysing X-ray intensities to distinguish a centre of symmetry.

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