

Harris R K. Comments on N.M.R. spectra of the $X_n AA' X_n$ type *Can. J. Chem.* 42:2275-81, 1964. [Mellon Institute, Pittsburgh, PA]

General expressions are derived for line positions and intensities in the X region of the NMR spectrum for an $X_n AA' X_n$ spin system in the case when long-range (X,X) coupling is negligible. Direct measurement of the spectra can usually give the coupling constants. [The *SCI*[®] indicates that this paper has been cited over 355 times since 1964.]

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"Nuclear magnetic resonance spectra for mobile isotropic solutions and liquids are unusual in that more-or-less exact simulation is frequently possible since the spin Hamiltonian is simple. Therefore the reverse process of obtaining the important molecular parameters (chemical shifts and coupling constants) by spectral analysis becomes feasible. Such spectral analysis became a great 'game' in the early 1960s because computers, which were frequently necessary to expedite the process, were becoming readily available. However, much of the skill in this 'game' resided in recognising spectral patterns and knowing how far they could be interpreted *before* seeking the help of a computer. I had become fascinated by this 'game' as a graduate student under Norman Sheppard at the University of Cambridge in the period 1959-62. This experience made me thoroughly inquisitive as far as other people's NMR spectra were concerned, and I frequently found myself saying to colleagues 'that would be a nice spectrum to analyze.' Almost as soon as I arrived at the

Mellon Institute, Pittsburgh, in 1962 as a research fellow, I made that statement to a new acquaintance there, Roy Hayter, who showed me a proton spectrum of tetramethyldiphosphine disulphide, $Me_3P(S)P(S)Me_3$. This looked particularly interesting because the spin system (comprising 1H and ^{31}P nuclei) is symmetrical, so group theoretical methods could in principle be invoked (though this proved not to be very important). Moreover, I had already done a little work on such a system at Cambridge for a totally different class of compounds (tetramethyl piperazines), so I set to work on the theory, using the assumption that long-range coupling between protons could be neglected. My resulting equations showed that full information could be derived from the spectrum very easily (without a computer!), and that the interpretation could be readily extended for similar symmetric spin systems with any number of protons, i.e., of the general type $X_n AA' X_n$. So a paper was written on the theory for the *Canadian Journal of Chemistry* (why this was chosen I cannot recall!) followed contiguously by one (written in collaboration with Hayter) on the application to tetramethyldiphosphine disulphide and related compounds.¹

"The work was carried out fairly light-heartedly. Indeed, it was a diversion from the research (on far infrared spectra) I was being paid for, and I am grateful to my research director, Foil Miller, for allowing it! I can claim no foresight in gauging its importance. The fact is that the spin system was found to be of extremely common occurrence, for a wide variety of chemical systems, but particularly for metal coordination compounds with two equivalent phosphorus-containing ligands, and the theory therefore was greatly used. I suspect that the large number of citations occurs partly because I was careful to point out the 'deceptive simplicity' of the spectra under certain limiting conditions, and many people have made use of such purely qualitative conclusions. Subsequent work has been reported in 'Subspectral analysis.'²

1. Harris R K & Hayter R G. Nuclear magnetic resonance studies of compounds related to tetramethyl diphosphine disulphide. *Can. J. Chem.* 42:2282-91, 1964.
2. Diehl P, Harris R K & Jones R G. Subspectral analysis. *Progr. Nucl. Magn. Res. Spectrosc.* 3:1-61, 1967.