# Determination of the Sign and Magnitude of $J$(XX) in [$A_nX$] $M_p$ Nuclear Spin Systems

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*Summary* A nuclear magnetic double resonance method for determining the sign and magnitude of $J$(XX) in $[A_nX]_2M_p$ spin systems by observation of the M resonance only is described, and is applied to some representative diphosphorus compounds.

In organophosphorus chemistry in particular, but also in other areas, it is often necessary to obtain spin coupling information from highly symmetrical nuclear spin systems. For the $[A_nX]_2$ system several methods have been proposed for obtaining the magnitude,[1] and in certain cases the sign also, of $J$(XX); of these the most versatile and convenient to use when $|J(XX)|$ is large is a double resonance one which involves the detection of weak lines in the X spectrum by observations of strong lines in the A spectrum.[2] For this method to succeed the A spectrum must be reasonably clearly resolved and uncomplicated (ideally, a deceptively simple triplet), but there are many situations when these conditions may not be fulfilled, *e.g.* if the A spins are protons in long chain alkyl groups or in phenyl groups in which the chemical shift differences between the *ortho-*, *meta-*, and *para*-positions are small. We now report that these difficulties may be avoided and the utility of the method greatly extended in molecules in which there are observable nuclei, M, symmetrically related and coupled to the X nuclei, but which need not necessarily be coupled to the A nuclei. When $J(AM) = 0$, the M spectrum will be a genuinely simple 1:2:1 triplet with repeated spacing $J$(MX) in which the outer components are associated with $\alpha\alpha$ and $\beta\beta$ spin states of the X spins. As a result of the magnetic asymmetry introduced by the A spins the X spectrum will have weak 'outer' transitions at positions which give $J$(XX) since they are the outer lines of *ab*-sub-spectra with coupling constants $J$(XX).[3] The weak lines to one side of $\nu_X$ arise from transitions involving the $\alpha\alpha$ spin states of the X nuclei; those to the other side involve the $\beta\beta$ spin states. Consideration of the energy-level diagram shows that these weak lines are connected with the two outer components of the M triplet. Irradiation of these outer transitions in the X spectrum using large values of $B_2$ to compensate for their low transition moments[4] will therefore perturb the M lines making it possible to determine $|J(\mathrm{XX})|$, and since any X transition will be connected with only one of the outer M lines, the sign of $J(\mathrm{XX})$ relative to that of $J(\mathrm{MX})$ will also be obtained.

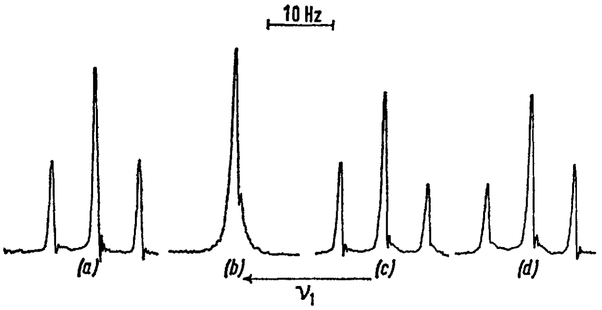

FIGURE. Frequency sweep 60 MHz $^1$H-{$^{31}$P} double resonance spectra of the *Pt*-methyl group of *trans*-[$(\mathrm{Me_2PhP})_2\mathrm{PtMeCl}$] at a constant amplitude, $B_2$, of the irradiating r.f. field; (*a*) $\nu_2$ set 10 kHz off-resonance, (*b*) $\nu_2 = \nu(^{31}\mathrm{P})$, (*c*) $\nu_2 = \nu(^{31}\mathrm{P}) - J(\mathrm{PP})$, (*d*) $\nu_2 = \nu(^{31}\mathrm{P}) + J(\mathrm{PP})$.

We give here three examples of applications of this technique to the determination of the sign and magnitude of $J(\mathrm{PP})$ in selected organophosphorus compounds.

(a) The molecule *trans* [$(\mathrm{Me_2PhP})_2\mathrm{PtMeCl}$] was chosen to check the validity of the method, since it was possible in this case to obtain the sign and magnitude of $^2J(\mathrm{PP})$ independently from $^1$H-{$^{31}$P} experiments solely upon the $[\mathrm{A_6X}]_2$ subsystem provided by the *P*-methyl protons and the phosphorus nuclei.[2] These experiments gave a value of 473 ± 6 Hz for $^2J(\mathrm{PP})$ and showed that its sign was opposite to that of $[^2J(\mathrm{PH}) + {}^4J(\mathrm{PH})]$ which was separately shown to be negative by comparison with $^1J(\mathrm{PPt})$ by $^1$H-{$^{195}$Pt} double resonance experiments. As expected, irradiation at $[\nu_\mathrm{P} \pm J(\mathrm{PP})]$, with an amplitude of $B_2$ large enough to produce significant decoupling when the irradiating field was centred on $\nu_\mathrm{P}$, produced asymmetry in the appearance of the *Pt*-methyl resonance and showed $^3J(\mathrm{PH})$ and $^2J(\mathrm{PP})$ to be of like sign (Figure). Since the former coupling is known to be positive from $^1$H-{$^{195}$Pt} experiments, it follows that $^2J$-(P–P) is positive in agreement with the result obtained previously from the $[\mathrm{A_6X}]_2$ sub-system. It was also found possible to determine $[\nu_\mathrm{P} \pm J(\mathrm{PP})]$ to ± 6 Hz solely from observations on the *Pt*-methyl resonance, and it is interesting to note that as $[^2J(\mathrm{PH}) + {}^4J(\mathrm{PH})]$ is of opposite sign to $^3J(\mathrm{PH})$, irradiation of any particular set of weak outer lines in the phosphorus spectrum gave asymmetries of opposite senses in the *P*-methyl and the *Pt*-methyl proton resonances.

(b) In the case of $\mathrm{Me_2C(PPh_2)_2}$, the spectrum of the phenyl protons was too complex to permit a direct determination of $^2J(\mathrm{PP})$, but coupling between the *ortho*-protons and phosphorus still gave the necessary magnetic non-equivalence. In fact, asymmetric perturbation of the methyl proton triplet was achieved at $\nu_\mathrm{P} + 120$ and $\nu_\mathrm{P} - 120$ Hz, and the sense of the asymmetry showed $^3J(\mathrm{PH})$ and $^2J(\mathrm{PP})$ to be of like sign, whence $^2J(\mathrm{PP}) = +\ 120 \pm 10$ Hz. This coupling was similarly found to be $(+45 \pm 5)$ Hz in $\mathrm{Me_2Si(PPh_2)_2}$.

(c) In the compound $\mathrm{MeN(PPh_2)_2}$, the phenyl proton resonances are fairly well spread out in some solvents, and it might have been possible to obtain $J(\mathrm{PP})$ from $^1$H-{$^{31}$P} experiments involving these signals alone. However, it was found very convenient to use the *N*-methyl triplet to detect the weak outer $^{31}$P lines and hence show that $^2J(\mathrm{PP}) = +\ 280 \pm 10$ Hz relative to a positive sign for $^3J(\mathrm{PH})$ (methyl).

These experiments, and several others which we have performed show that this technique is a valuable development of the double resonance method originally proposed for the study of this type of system. It will be extendable to other more complex systems and it greatly increases the range of molecules from which useful data can be obtained. It is important to realise that the precise origin of the magnetic asymmetry is not significant, and in principle it should be possible to study $\mathrm{X_2M}_p$ systems having any feature leading to the effective chemical shift differences which produce transitions near $[\nu_\mathrm{X} \pm J(\mathrm{XX})]$. An example might be quadrupolar broadening of the phosphorus resonances by direct bound $^{35/37}$Cl, although we have not yet realized this experimentally.

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