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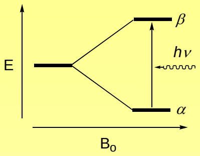
The *para*-Hydrogen Phenomenon, A Chemical Perspective

Introduction

Most spectroscopic techniques involve the observation of transitions between quantum states in molecules (Fig 1). Nuclear magnetic resonance (NMR) spectroscopy examines transitions between nuclear spin states. Whilst NMR spectroscopy is an extremely versatile tool for the characterisation of molecules and the study of their reactivity, it does have a major limitation.

Fig 1. Basic energy level diagram for NMR spectroscopy



The intensity of the NMR absorption depends largely on the population difference between the ground and excited nuclear spin state orientations in the sample. In NMR, the difference in energy between the spin states of nuclei is due to their interaction with an applied magnetic field and is small in comparison to the available thermal energy. As a consequence, the Boltzmann populations of the α and β states of hydrogen nuclei have a difference of only 1 in 31,000 in the magnet of a 400 MHz spectrometer. Hence, effectively only *ca.* 10^{-4} of the available sample can be interrogated and so NMR is said to be an inherently insensitive technique.

What is *para*-Hydrogen?

The wavefunction that describes the dihydrogen molecule has translational, rotational, vibrational, electronic and nuclear contributions and must be anti-symmetric overall.

$$\psi_{H_2} = \psi_{trans}\psi_{rot}\psi_{vib}\psi_{elec}\psi_{nuc}$$

The partition functions for the vibrational and electronic contributions to the overall wavefunction are symmetric. Since neither $\alpha_{Ha}\beta_{Hb}$ or $\beta_{Ha}\alpha_{Hb}$ spin state orientations of H_2 are symmetric or anti symmetric to label interchange, linear combinations must be taken. Dihydrogen nuclei exhibiting the anti-symmetric combination, $(\alpha\beta - \beta\alpha)$, are termed *para*-hydrogen and restricted to even values of J.[1,2]

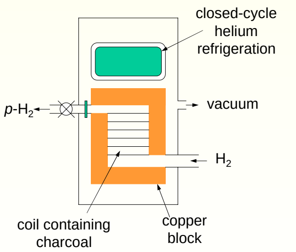
ψ_{nuc}	ψ_{rot}
$\alpha\alpha$ $\beta\beta$ $\alpha\beta + \beta\alpha$	J = 1,3,5… *ortho*-H_2
$\alpha\beta - \beta\alpha$	J = 0,2,4… ***para*-H$_2$**

p-H_2 is therefore energetically more stable than *o*-H_2 (the three symmetric forms) as it can access the $J = 0$ state.

How is *para*-Hydrogen Generated?

The nuclear spin state of a hydrogen molecule ordinarily can not be changed from *ortho* to *para* as this requires a concomitant change in rotational state and so is forbidden. However, such a spin transition can be facilitated by interaction with, for example, a paramagnetic surface. Hence if H_2 is cooled to 20 K over such a surface, spin transitions can occur allowing H_2 to access it's preferred Boltzmann distribution based on rotational states, i.e. $J = 0$, hence generating virtually pure *para*-H_2. This can then be removed and allowed to warm to give an "indefinitely" stable pure spin state.

Fig 2. Schematic diagram of *para*-hydrogen generation apparatus



Temperature / K	% *ortho*	% *para*
273	75	25
150	71	29
77	48	52
20	0.2	99.8

Fig 3. *Para*-hydrogen generation rig.

Why use *para*-Hydrogen?

Dihydrogen can react with transition metal compounds to form metal dihydrides. If the two new hydride ligands are magnetically inequivalent, four energy levels describe the hydrogen nuclei spin states. This results in the observation of two doublet signals in the NMR spectrum (Fig 4a).

If, however, *para*-hydrogen is used in the reaction, and the two nuclei transfer to the metal in a pairwise manner, then the αα and ββ spin states of the product are not populated (Fig 4b). Hence, use of *para*-hydrogen allows the selective chemical synthesis of a non-Boltzmann spin state population in the product. Interrogation of the sample results in the observation of large signal enhancements (up to the theoretical maximum enhancement of 31,000 fold for a 400 MHz machine). The signals appear as characteristic anti-phase doublets due to absorption and emission transitions from populated unpopulated states.

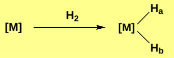
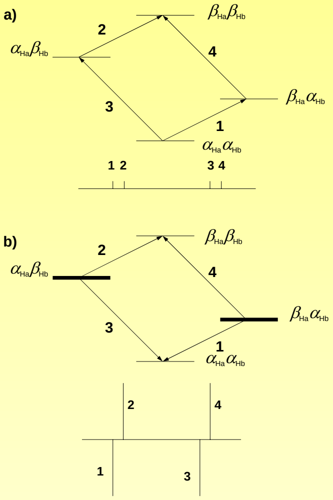
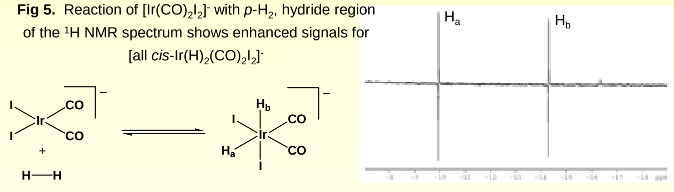


Fig 4. ^{1}H spin system for metal dihydride, a) normal H_2, b) *para*-H_2



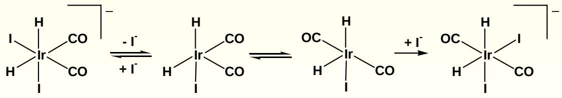
An example of the use of *para*-hydrogen is provided by the observation of the previously undetected species [all *cis*–$Ir(H)_2(CO)_2I_2]^-$ formed from addition of *p*-H_2 to the iridium(I) complex, $[Ir(CO)_2I_2]^-$ (Fig 5).[3]

Fig 5. Reaction of $[Ir(CO)_2I_2]^-$ with *p*-H_2, hydride region of the ^{1}H NMR spectrum shows enhanced signals for [all *cis*-$Ir(H)_2(CO)_2I_2]^-$



The use of *p*-H_2 in the detection of this species also allowed the study of its isomerisation reactivity (Fig 6) and activation parameters for the reductive elimination of H_2 to be obtained ($\Delta H^\ddagger$ = 106 ± 10 kJ mol^{-1}, $\Delta S^\ddagger$ = 60 ± 6 J K^{-1} mol^{-1}) by ^{1}H-^{1}H EXSY spectroscopy.

Fig 6. Isomerisation reactivity of [all *cis*-$Ir(H)_2(CO)_2I_2]^-$



Conclusions

Use of *para*-hydrogen allows the generation of products with non-Boltzmann spin populations and hence enhanced signal intensity. This phenomenon facilitates the observation of otherwise undetectable species such as low concentration intermediates in catalytic reactions, species occurring in minor reaction pathways and species that are minor constituents of H_2 addition equilibria. *Para*-hydrogen induced polarisation (PHIP) enhanced NMR spectroscopy can therefore provide valuable insight into the mechanisms of catalytic reactions and the identification of minor competing side routes.

References

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3. Hasnip, S.K., Duckett, S.B., Taylor, D.R., Barlow, G.K., Taylor, M.J., *Chem. Comm.*, **1999**, 889.