This project concerns the study of the interconversion dynamics of nuclear spin isomers of small molecules using high resolution optical spectroscopy. Molecules of high symmetry containing magnetically active centers exist in energetically distinct nuclear spin configurations. In the case of molecular hydrogen, there are four allowed spin configurations: The first three, \( \alpha\alpha, \beta\beta \) and \( \alpha\beta+\beta\alpha \), are triply degenerate and symmetric with respect to the exchange of nuclei and comprise the ortho-\( \text{H}_2 \) spin-isomer. The remaining configuration, \( \alpha\beta-\beta\alpha \), is antisymmetric with respect to exchange of nuclei and known as para-\( \text{H}_2 \). These spin configurations lie extremely close together in energy, and all four are populated essentially equally at room temperature.

ortho-\( \text{H}_2 \) can be thought of as having the two spins aligned with a net magnetic moment and can be therefore be seen in an NMR experiment. In para-\( \text{H}_2 \), however, the spins are opposed and cancel out, making it invisible to NMR unless the symmetry of the molecule is somehow broken. However, when para-\( \text{H}_2 \) reacts with a substrate, it does so in a spin-correlated manner and selectively populates only one of the spin states in the product. The resultant hyperpolarisation, a term used to indicate the populations of each energy level are greatly different to the usual Boltzmann distribution, causes the NMR signals of the product to be increased to quite extraordinary extents. Such processes have particular topical importance in magnetic resonance imaging applications.

Although the interconversion of different spin isomers is symmetry forbidden, it can be achieved using a catalyst, and consequently, pure samples of para-\( \text{H}_2 \) can be generated relatively easily. Such spin modifications can similarly be achieved in polyatomic molecules with two or more identical and equivalent nuclei. Thus, \( ^{15}\text{N}_2 \), \( \text{H}_2\text{O} \) and \( \text{H}_2\text{CO} \), have ortho \( (I = 1) \) and para \( (I = 0) \) forms; \( \text{NH}_3 \) and \( \text{CH}_3\text{F} \), have ortho \( (I = 3/2) \) and para \( (I = 1/2) \) forms; and \( \text{CH}_4 \) has ortho \( (I = 1) \), meta \( (I = 2) \), and para \( (I = 0) \) forms. These different spin isomers can be identified spectroscopically through rotational line intensity modulations seen in appropriate gas phase molecular spectra. High resolution optical spectroscopy can therefore provide a detailed understanding of how such isomers interconvert and on their relaxation dynamics and we hope will provide one of the keys to the successful future development of hyperpolarisation technology.