P004 Coherent Raman detected electron spin resonance spectroscopy: A "double resonance" technique linking electron spin resonance and magnetic circular dichroism.

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The simultaneous excitation of paramagnetic molecules with optical (laser) and microwave radiation can cause an amplitude or phase modulation of the transmitted light at the microwave frequency. The detection of this modulation indicates the presence of coupled optical and electron spin resonance (ESR) transitions. Physically, the phenomenon can be viewed as a coherent Raman effect or, in most cases, as a microwave frequency modulation of the magnetic circular dichroism by the precessing magnetisation. Although commonly referred to as coherent Raman detected ESR, this name is unsatisfactory because the true power of the method stems principally from its ability to correlate the optical and magnetic properties of a molecule, rather than merely to detect the latter. Such correlations offer two powerful capabilities of relevance to biological spectroscopy. Firstly, it is possible to exploit the enhanced chemical selectivity of the method to deconvolute the overlapping optical or ESR spectra of multiple chemical species in a sample, or multiple centres in a protein. Secondly, it is possible, through spectral "powder" lineshape simulation, to deduce the relative orientations of the magnetic and optical anisotropies of each species, even when the species cannot be obtained in a crystalline sample. Such measurements will provide challenging new constraints for modern electronic structure calculations. The capabilities of coherent Raman detected ESR will be illustrated by data from proteins containing copper and haem centres.