

In recent years studies of free radicals in the gas phase by electron paramagnetic resonance have mainly used microwave sources in the X-band (ca. 9000 MHz) and the molecules detected have been almost exclusively diatomics in $^2\Pi$, $^3\Sigma$ or $^1\Delta$ states. In recent years, for instance, we have studied $\text{OH}(^2\Pi, \nu = 1-5)$, $\text{S}_2(^3\Sigma_g^-)$ and $\text{NF}(^1\Delta)$. This spectral region has, however, proved less useful for polyatomic species and for linear molecules in $^2\Sigma$ states.

However, if the microwave source is replaced by a far infra-red laser operation in the $30-120\text{ cm}^{-1}$ range, the Zeeman effect can be used to bring a rotational transition of a free radical into resonance the laser line providing their initial separation does not exceed 2 cm^{-1} . If the free radicals are generated within the laser cavity, the greater energy of the transitions increases the sensitivity by a factor of 1000 as compared with gas phase e.p.r. This is due to the increased transition probability and to the greater difference between the populations of the levels involved. Parallel and perpendicular transitions can be separated by rotating the plane polarisation of the laser beam.

Analysis of laser magnetic resonance spectra can provide structural information about free radicals. Spectra of the ground states of NH_2 and PH_2 are presented, together with spectra of $\text{PH}(^3\Sigma^-)$ and $\text{PH}(^1\Delta)$. The unpaired electron(s) in PH_2 and $\text{PH}(^1\Delta)$ are shown to be largely localised on the $3p$ orbital of the P atom.

This work has been carried out in collaboration with Drs. P. B. Davies, D. K. Russell and F. D. Wayne.

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Photochemically Induced Dynamic Magnetic Polarization

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The current theories of chemically induced dynamic magnetic polarization in free radical reactions in carbonyl photochemical systems are summarized in terms of the "radical-pair" and the photoexcited triplet models. Experimental evidence is presented to show the co-existence of both these mechanisms in electron as well as in nuclear polarization. Systematic and correlated CIDEP and

CIDNP investigations of the photochemical reactions of quinones and aliphatic carbonyl compounds allow the introduction of a general scheme for the simultaneous operations of the two mechanisms in the photochemical systems. The primary photochemical reactions contribute to magnetic polarization via the "photoexcited triplet" model, whereas the secondary reactions of the primary radical-pair contribute by the "radical-pair" mechanism. Detailed analysis of the magnetic polarization results would lead to important information on dynamics and mechanisms of intersystem crossing, rates of chemical reactions of the triplet sublevels and the spin-lattice relaxation rates of the triplets and the transient radicals in solution.

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Modulated Excitation ESR Spectra of Hydroxy-Phenoxy Radicals

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In a modulated excitation E.S.R. (M.E.S.R.) spectrometer the UV light inducing the photochemical reaction is sinusoidally modulated, so that beside the conventional E.S.R. of the resulting radicals also the phase shift and amplitude of each individual line of the spectrum can be measured. The detection system [1] of such an instrument is schematically shown in Fig. 1.

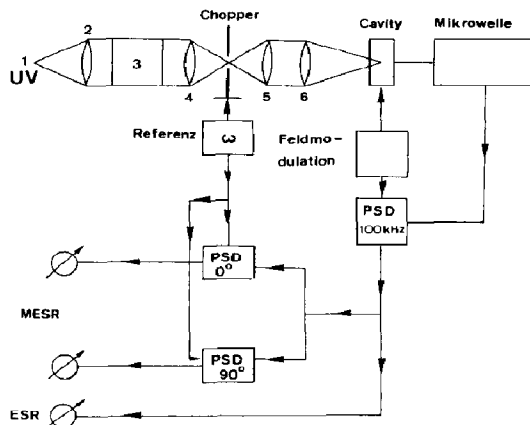


Fig. 1. Detection system of the M.E.S.R. spectrometer.