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 $OH(^2\Pi, v = 1$ - $5)$, $S_2(^3\Sigma_g^-)$ and $NF(^1\Delta)$. 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 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 $PH(^3\Sigma^-)$ and $PH(^1\Delta)$. The unpaired electron(s) in PH_2 and $PH(^1\Delta)$ 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.

P6
Photochemically Induced Dynamic Magnetic Polarization

J. K. S. WAN
Department of Chemistry, Queen's University, Kingston, Ontario (Canada)

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 coexistence 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.

P7
Modulated Excitation ESR Spectra of Hydroxy-Phenoxy Radicals

K. LOTH, F. GRAF and Hs. H. GÜNTHARD
*Laboratory for Physical Chemistry ETH,
Universitätstrasse 22, CH-8006 Zurich
(Switzerland)*

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.
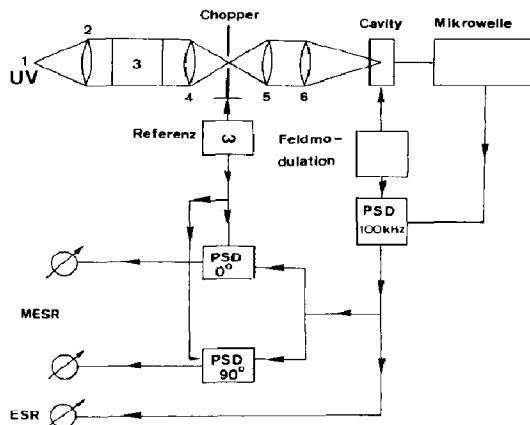

Fig. 1. Detection system of the M.E.S.R. spectrometer.

Analysis of the experiments is based on a kinetic model consisting of a Jablonski diagram with irreversible first order reactions departing from the excited singlet and triplet states (*cf.* Fig. 2).
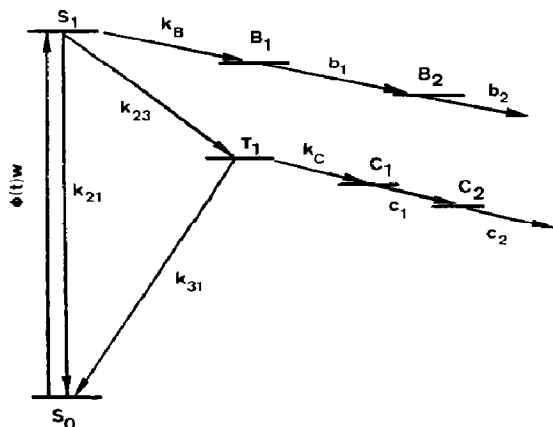

Fig. 2. Kinetic model.

Solutions of the corresponding system of differential equations may be analytically obtained [2] and exhibit a frequency dependence of amplitude and phase typ-

ical for electrical RC networks [3]. As a result, the modulated excitation method as a counterpart of single shot techniques, may be successfully used for

— determination of lifetimes of radicals
— determination of sequences in multiple step reactions
— discrimination between first and second order kinetic processes.

Figure 3 shows the amplitude and phase of the modulated ESR spectrum of the 2,6-dihydroxyphenoxy radical as a function of modulation frequency (the so called Bode representation is used phase shift and log amplitude *vs.* log exciting frequency). From this Figure, the following conclusion about the radical may be immediately drawn:

— the system is linear (no second order reactions)
— the radical is the first detectable particle in the chain (asymptotically the phase shift amounts to $-90°$ and the amplitude decreases with 6db/octave)
— the lifetime τ of the radical under the conditions of the experiment is 3.3 ± 0.3 ms.
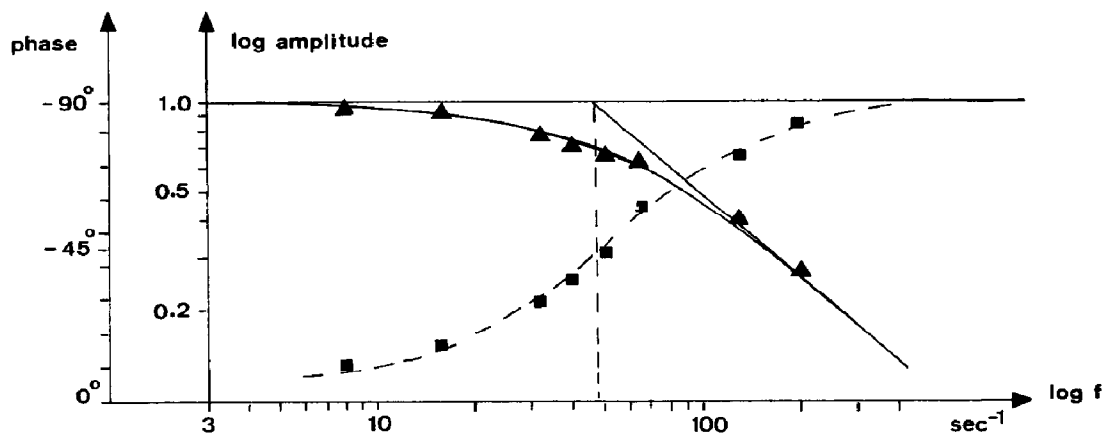

Fig. 3. Phase shift and log amplitude plotted against log excited frequency.

1 K. Loth, F. Graf and Hs. H. Günthard, Chem. Phys. Letters, 29 (1974) 163.
2 M. Forster, U. P. Fringeli and Hs. H. Günthard, Helv. Chim. Acta, 56 (1973)389
3 M. S. Ghausi, Principle and Design of Linear Active Circuits, McGraw-Hill, New York, 1965, Ch. 2.