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Emission Electron Spin Resonance Spectra from Free Radicals in Solution

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Summary The emission e.s.r. spectra of free radicals produced by laser flash photolysis in solution are reported.

WE have described elsewhere a technique that enables the e.s.r. spectrum of free radicals to be observed throughout their lifetime from 1 μsec after formation.[1] We report that, in several cases, the entire e.s.r. spectrum appears in emission immediately after the formation of the radicals and that within a few microseconds the emission decays, to be replaced by the corresponding absorption.

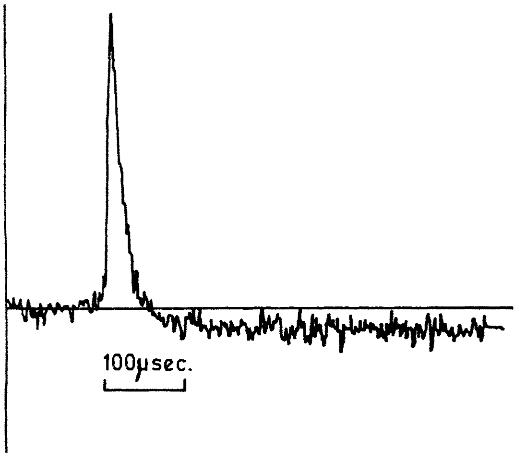

FIGURE 1. *Time dependence of the amplitude of the e.s.r. spectrum of the radical from 2-chlorobenzaldehyde in liquid paraffin.*

The technique employs the observation of the amplitude of the signal as a function of time at a fixed magnetic field. By recording the signal at various magnetic fields, an e.s.r. spectrum of amplitude as a function of field at a given time may be extracted from a profile of the decay curves at that time.[1] At present, the shortest time at which the spectrum may be observed is about 5 μsec. In the experiments reported here, a flash from a nitrogen gas laser operating at 337·1 nm is used to produce the radicals. The time dependence of the amplitude of a typical e.s.r. spectrum (2-chlorobenzaldehyde in liquid paraffin at room temperature) is illustrated in Figure 1. The phase of the signal changes with a time constant of about 14 μsec into an absorption which decays with a half-life of about 2·4 msec as a result of chemical reaction. As the magnetic field is varied, the amplitude and phase of the signal changes: Figures 2a and 2b show the profile of the curves in emission and absorption, respectively. The former appears to be the same as the latter except for its opposite phase and improved signal-to-noise ratio (the relative intensities of the spectra in the diagram are arbitrary). Emission has been observed in benzophenone, benzaldehyde, 2- and 4-chlorobenzaldehyde, acetophenone, dibenzil, and anthraquinone. Some molecules containing the carbonyl group

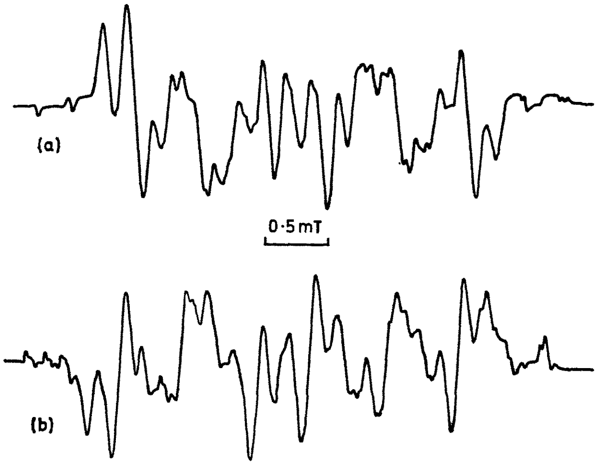

FIGURE 2. *Total spectrum of the radical from 2-chlorobenzaldehyde observed in* (a) *emission and* (b) *absorption.*

do not show emission, but this may be due to a very short relaxation time.

The emission is most unlikely to be a spurious effect of the equipment since it depends on the field and the solvent, and is not shown by all radicals. Furthermore, the laser radiation travels perpendicular to the static magnetic field and is not polarized. The mechanism of the population inversion is not fully understood but probably occurs in one of the reaction steps following the primary absorption. The radicals might be produced as follows: on irradiation, singlet to singlet ($\pi^* \leftarrow n$) absorption occurs, followed by intersystem crossing to the lowest triplet; electron extraction and, where possible, proton extraction from solvent occurs, to form the doublet species. Although the intersystem crossing is governed by selection rules which in solids lead to population differences of the type we have observed,[2,3] it is difficult to conceive how the same selection rules could lead to population inversion in a freely rotating radical in solution. It is possible that electron extraction from the solvent proceeds by a tunnelling process preferentially into the level of the triplet closest to the top of the barrier, and so leads to a doublet radical with inverted population, but the energy differences involved are small. If the radicals from the solvent and solute are initially spin saturated and strongly coupled a dynamic polarization of the latter may occur if the former relaxes rapidly to equilibrium. Such a mechanism with coupling through $s_1^{\pm}s_2^{\mp}$ terms in the interaction Hamiltonian will invert the population of the solute radicals, and their spectra will appear in emission. The observed enhancement factor of about 5 would then need to be explained in terms of the enhancement being greater than the polarization (as in the Overhauser effect) or in terms of an initially rapid radical decay.

We stress that the emission is observed for all the hyperfine lines, in contrast to the situation observed by Smaller *et al.* in which one half of the spectrum was in emission and the other half in enhanced absorption, which can be explained in terms of a simple spin-pumping mechanism.[5]

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