

FREE RADICAL PHENOMENA

IN

IRRADIATED ORGANIC CRYSTALS

By

D.R. Cutten B. Sc. (Hons.)

A Thesis

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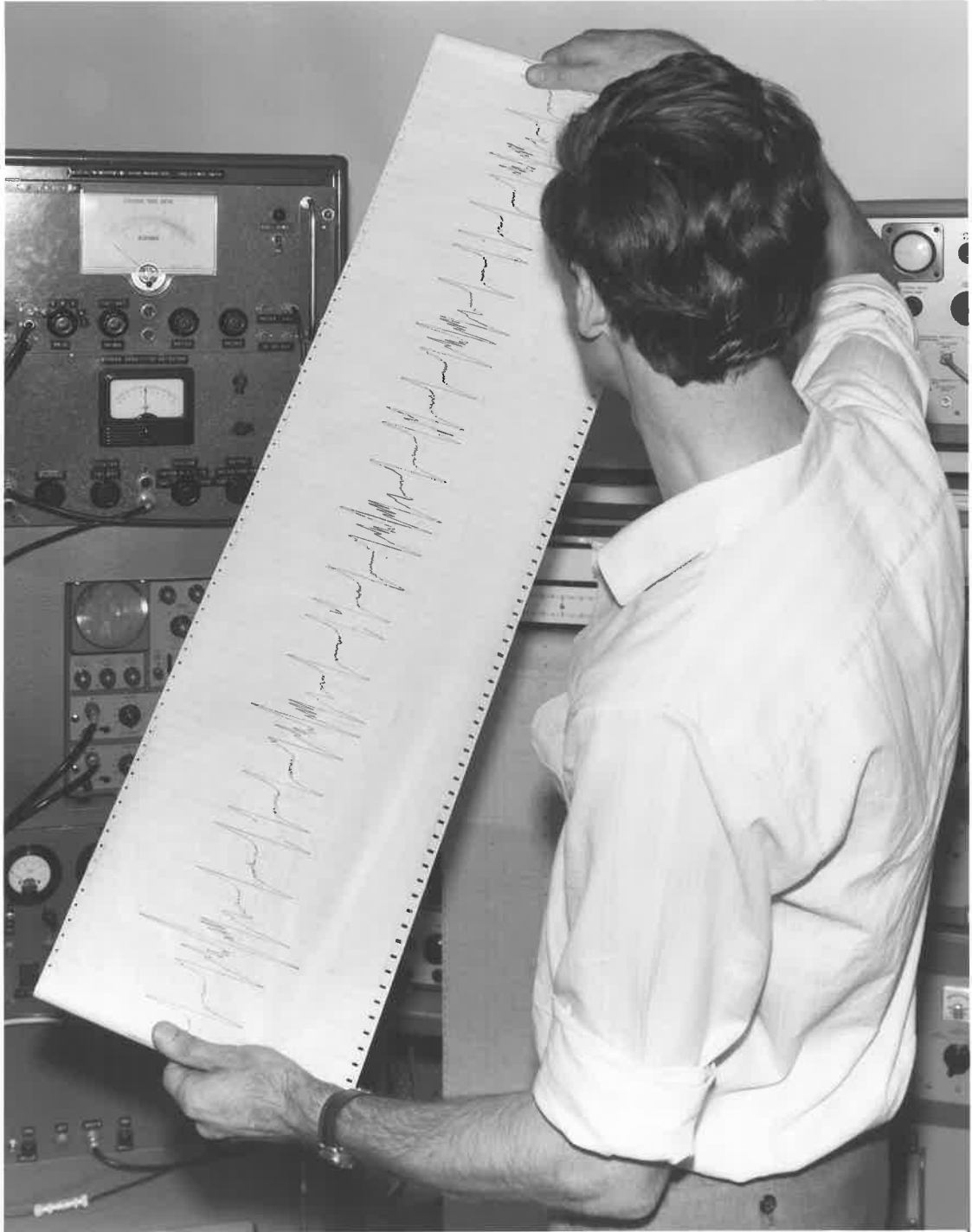
in the

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## FRONTISPIECE

Shows the author examining a series of E.S.R. spectra  
obtained from an irradiated succinic acid crystal  
during its annealing.

## SUMMARY

The thesis describes an experimental and theoretical investigation of the behaviour of free radicals in irradiated organic single crystals. Attention is confined to problems concerned in the production and post-irradiation behaviour of free radicals as distinct from previous work which has been concerned mainly with problems of their identification and interpretation of their ESR spectra. The work centres around the problem as to whether mobile hydrogen atom vacancies play a role of any importance in free radical behaviour and especially in their thermal annealing. In this regard the literature has been reviewed and a search made for evidence implicitly related to this question. The necessary and reasonable consequences of the hydrogen atom vacancy being readily mobile have been analysed in some detail to provide a guide to experiments aimed at the verification of this hypothesis. A by-product of this part of the work is the proposal of a new and convenient nomenclature for complex organic radicals.

The thesis describes apparatus designed and constructed in the course of this work, the most important of which is a variable temperature cavity enabling the thermal behaviour of free radicals to be observed at elevated temperatures.

Experimental studies showed the production rates of free radicals and their rates of thermal annealing to be quite reproducible from specimen to specimen to an extent indeed, beyond what one expects for reactions in the solid state. The kinetics of free radical thermal destruction was investigated in selected systems; reaction kinetics were found to be usually second-order; activation energies were measured where possible. Selected cases were examined for the deuterium isotope effect on reaction rates

which was found in two instances. Several systems were examined by means of differential infrared spectroscopy for evidence of the phenomenon known as "isotopic mixing". This was found to occur in one case (viz  $OO^2$  - dideuteriosuccinic acid single crystal) to such an extent that it is easily observed in the infrared spectra. Other techniques (namely differential thermal analysis, free radical production by hydrogen atom bombardment and macroscopic diffusion measurements) were employed on account of their relevance to these problems.

The general conclusion of the thesis is that the hydrogen atom vacancy probably does play a major role in post-irradiation behaviour of organic free radical phenomena. The best new evidence brought forward, for <sup>at least</sup> the occasional relevance of this mechanism, is the abovementioned occurrence of large scale isotopic mixing in partially deuterated succinic acid single crystal. However, it seems likely from the evidence that it is not the sole mechanism which provides the radical state mobility necessary to explain the thermal annealing of free radicals at moderate temperatures.

## PREFACE

The text of this thesis, except where due reference is made, describes the original and personal work of the author which was carried out between January, 1964, and September, 1968, in the Physics Department of the University of Adelaide. No material contained in this thesis has been submitted for a degree or diploma in this or any other university.

D.R. Cutten  
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