

Preface

At the time of his death in April, 2004, Professor Philip H. Rieger had nearly finished the manuscript of this book. His intention was to present a monograph summarizing his approach to the field of Electron Spin Resonance using examples and other explanatory material developed during the course of a 40-year career of research and teaching at Brown University. Although the presentation was intended to be at the beginning graduate level, it could also serve as an introduction to the fundamentals of ESR for working research scientists in organometallic chemistry or other areas from which Phil attracted his many research collaborators. It gives the reader a thorough introduction to the analysis and interpretation of CW ESR spectra at X-band (9.5 GHz.) as applied to paramagnetic organic, inorganic and organometallic molecules.

When Professor Rieger first became interested in ESR, commercial instruments were not available. His introduction to the field, as a graduate student with George Fraenkel at Columbia University, took place in one of the few laboratories in the world at the time where ESR equipment had been built. Upon arriving at Brown his first item of business was to design and construct a spectrometer. The instrument was eventually retired once reliable, sensitive commercial instruments became available. Nevertheless, that first spectrometer enabled one of us (ALR) to begin a scientific collaboration that lasted the rest of Phil's life, and the other (RGL) to get his own career started at Brown.

In a preliminary draft of this book Phil wrote the following paragraph explaining its origin:

This book has been many years in the making. It began with an invitation from Prof. William Trogler to write a chapter on ESR applications for the book *Organometallic Radical Processes* that was published in 1990. There are some strong resemblances to Chapter 4 of the present book. The writing was extended to a handout in 1991 when I was invited to spend a sabbatical year at the University of Bristol. It was extended a bit further when I was invited to give a series of lectures on ESR at the University of Oviedo, still further when I was invited to give some lectures at the University of Edinburgh, and still further in 1999 for a lecture series

at the University of Otago. Meanwhile, I had given a short series of lectures on ESR at Brown University most years as part of a graduate course in Physical Inorganic Chemistry.

In completing Phil's book we have retained the set of examples and explanations, and occasional commentary, as he had intended it. It has, however, been some time since a book on ESR for the non-expert has appeared. We have therefore supplemented his original manuscript in two ways. At the end of Chapter 1 is added an up-to-date list of texts and monographs on ESR which should serve the interested reader as a source of additional treatments of the subject. Secondly, in Appendix 2 we have referenced and given brief descriptions of some advanced ESR methods that have been developed in recent years and applied in various fields, including biochemistry. The modern ESR spectroscopist is now as likely to need an understanding of these techniques as of the classic X-band methods described here. We hope that this book will provide a basis for study of the newer methods.

One of Philip Rieger's most important contributions to the field of ESR, and the motivation for much of his collaborative research, was his instinctive understanding of how to analyze the powder patterns of paramagnetic inorganic complexes, often using programs for simulating and analyzing such spectra that he had developed over the years. A summary of his work in this area may be found in a review titled "Simulation and analysis of ESR powder patterns" published in the Specialist Periodical Report *Electron Spin Resonance*, Royal Society of Chemistry, Cambridge, 1993, vol 13B, ch. 4, pp. 178–199. Specism and other ESR tools written by Prof. Rieger are available from the Manchester University website at www.epr.chemistry.manchester.ac.uk. When you go to this site you will find a menu on the left with a 'Software' button which will give you access to this material.

We are particularly grateful to Elsevier Publishing Company for allowing the use, and modification, of material that originally appeared in *Organometallic Radical Processes*, *Journal of Organometallic Chemistry Library*, ed. W. C. Trogler, Elsevier, Amsterdam, 1990, vol 22. Most of Chapter 4, and also substantial parts of Chapter 3, were first published in this review. Other reviews by Professor Rieger on topics covered in this book include "Electron paramagnetic resonance studies of low-spin d^5 metal complexes", *Coord. Chem. Rev.*, 1994, **135**, 203; "Chemical insights from EPR spectra of organometallic radicals and radical ions" (with Dr. Anne L. Rieger), *Organometallics*, 2004, **23**, 154; and "Electron spin resonance", in *Physical Methods of Chemistry*, ed. A. Weissberger and B. W. Rossiter, John Wiley and Sons, Inc., New York, 1972, Part IIIA, ch.VI, pp 499–598.

Anne L. Rieger (Mrs. Philip Rieger) is grateful to Brown University for providing her with the facilities to make the completion of this project possible: office space, computers, the use of libraries, and a high speed internet connection to Professor Lawler in the mountains of New Hampshire. For many years Professor Rieger was associated with the ESR group of the Royal Society of Chemistry. The support and encouragement of many members of the group has

served as an impetus to see this project to completion and is gratefully acknowledged. Professor Neil Connelly of Bristol University, a long time collaborator and friend, has also contributed to the completion of the project and his input is very much appreciated. Finally, Ron Lawler is grateful to Margaret Merritt for her advice and support during this occasionally frustrating, but always interesting, introduction to the world of desktop publishing. We hope that our friend, companion and colleague Phil would be pleased with the result.

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