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Preface

Why another book on NMR?

The NMR school in Florence is now 30 years old. The founder was the senior author (I.B.) under the patronage of his professor, Luigi Sacconi. The junior author (C.L.) belongs to this school. He is professor in Bologna where he has labs and pupils, but is also associated with the Florence NMR lab through an interuniversity consortium. The Florence lab has been recognized as a Large Scale Facility of the European Community (1993–1996) and as a Large Scale Facility of the European Union (1996–1999).

These recognitions have exposed the lab to many visitors and to many intellectual challenges in the field of NMR of paramagnetic molecules. We have pursued research in the field of electron and nuclear relaxation at room temperature, and handled the effect on nuclear relaxation of zero field splitting, of the splitting of the *S* manifold due to coupling with the metal nuclei, and to magnetic exchange due to coupling in polymetallic systems. Several of these achievements can be found in the book we have written in collaboration with Lucia Banci "Nuclear and Electron Relaxation" (VCH, Weinheim, 1991). Previously, we had written the book "NMR of Paramagnetic Molecules in Biological Systems" (Benjamin/Cummings, Menlo Park, 1986); now we have succeeded in solving the solution structures of paramagnetic metalloproteins. By introducing fast nuclear relaxation in NMR spectral simulations we believe we have succeeded in bringing the field of NMR of paramagnetic molecules into the main field of NMR, with the advantage of exploiting new sources of information such as electron spin density distribution, pseudocontact shifts and electron–nucleus dipolar coupling.

We now want to share our experience with researchers in the field. This book is the result of this effort.

Someone may object that spin density delocalization and contact shifts are now classical subjects, with little novelty. And assuredly there are people (although few!) who have mastered these theoretical aspects a long time ago. We have treated this subject in Chapter 2, with the aim of providing the reader with a modern but simple point of view. Here we have tried to describe the pseudocontact shift in a pictorial way and have presented a simplified way of calculating it (Appendix III). We are grateful to Bruce McGarvey for his many helpful suggestions, including those given on the contents of Chapters 1, 5 and 8.

In Chapter 3 we have treated nuclear relaxation as it depends on being coupled with electrons. Seymour H. Koenig, an outstanding pioneer in the field, has proved a blessing. We owe him a lot, including many discussions over the last eighteen years. Robert G. Bryant has also competently discussed this chapter. Chapter 3 covers a solid and by now classic piece of theory which, however, is still not very popular. The understanding of the principles of nuclear relaxation when the nucleus interacts with unpaired electrons is of basic importance for pursuing research on contrast agents for magnetic resonance imaging.

Chemical exchange is a broad, difficult, and (to some) boring subject. We have tried to highlight some aspects which need attention when related to paramagnetic species. Jozef Kowalewski has commented on this chapter. The similarity between cross relaxation and chemical exchange is stressed as far as nuclear relaxation is concerned. The consequences of chemical exchange on the magnetization recovery profile after a perturbation are also stressed.

In Chapter 5, a speciality of our lab is treated. The chapter deals with the shift and relaxation properties of magnetically coupled systems. One can object that we have already written so much in this area that there is no need for this further contribution. However, on the one hand the subject is difficult, and on the other our previous writings have not totally succeeded in popularizing it. This is why we insist! Finally, polymetallic systems significantly broaden the field of application of this spectroscopy.

In Chapter 6 we deal with the Overhauser effect, relaxation rates, and cross relaxation. We have picked out the features which distinguish experiments of Overhauser effects in paramagnetic systems from those in diamagnetic systems. Indeed, paramagnetic relaxation may quench cross relaxation; saturation of a fast relaxing nucleus and observation of NOE on a slow relaxing nucleus makes 1D NOE measurements superior to a 2D NOESY approach. Finally, this chapter revisits the foundations of the nucleus–nucleus dipolar interactions in a hopefully simple way. Comments by N. Murali on this chapter have been extremely useful.

2D experiments in paramagnetic systems are treated in Chapter 7. Here we provide the tools to plan pulse sequences and time delays suitable for paramagnetic systems. In Appendix V we summarize how product operators can be used to understand pulse sequences, and give some hints for the simulation of spectra by also including nuclear relaxation. This appendix has been written in collaboration with Antonio Rosato, a brilliant student who is familiar with the physics of NMR. Chapter 7 and Chapter 9, in which we give some advice on how to perform as successful NMR spectroscopists on paramagnetic systems, represent the core of the book for experimentalists. Here we try to make clear that the NMR of paramagnetic molecules may be superior, in terms of information obtained, to diamagnetic systems if the electronic relaxation times are not overly long. We are thankful to the following for comments and suggestions: Q. Teng for Chapter 7, and Li-June Ming for Chapter 9.

Chapter 8 deals with NMR of solids. We are not specialists in this field, and at times we may seem rather naive. This chapter has Silvio Aime as coauthor. At least he is familiar with solid state NMR!

As usual in our books, we use SI units throughout. They are particularly useful when dealing with magnetic interactions. Some readers may have to adjust to the fact that dipolar interactions depend on reciprocal cubic meters, and that molecular magnetic susceptibilities are expressed in cubic meters. However, they should at least appreciate how easily a dimensionless shift is obtained when dividing susceptibilities by cubic meters! Sometimes we have left the ångström as an abbreviation for 10^{-1} m.

Our colleague Gabriele Spina, and Drs Oleg Galas, Giacomo Parigi and Antonio Rosato read the manuscript. To them goes out gratitude.

We have a saying in Italy: if these bushes are roses they will bloom ...