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Chlorine, Bromine and Iodine NMR

Physico-Chemical and
Biological Applications

With 74 Figures



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Editorial

Since the series "NMR - Basic Principles and Progress" was founded in 1969 it has dealt primarily with the theoretical and physical aspects of the methods. Today nuclear-magnetic resonance spectroscopy has become one of the principal techniques of the chemist and is finding increasing use in the fields of Biology, Pharmacy, Medicine, and Criminology. The growing significance of applied spectroscopy has earned it a correspondingly important place for the future in this series. With the aim of achieving a balanced representation of theoretical and practical problems and results, the present Editors have asked several world-renowned scientists in the field of NMR spectroscopy to join an International Editorial Board.

The international nature of this Board will facilitate closer contact among research groups and authors throughout the world, making it possible to follow comprehensively the developments in pure and applied NMR spectroscopy. On this basis, the readers of the series will be assured of up-to-date contributions not only of current significance, but of long-term value as well.

Prof. E. Fluck, Prof. P. Diehl, Prof. R. Kosfeld, 1976

Preface

The increasing interest in NMR spectroscopy of what in some conferences in this field is commonly termed "other nuclei" is unmistakable. Chemists and biologists who employ NMR spectroscopy to study their problems have, however, been somewhat reluctant to study nuclei with electric quadrupole moments. These nuclei frequently give rise to broad NMR signals, sometimes too broad to be detectable with ordinary high resolution NMR spectrometers. Spectrometers that could cope with broad NMR signals of low intensity, "wide-line" spectrometers, have been available since the mid 1950:s but it appears that most of these instruments ended up in physical laboratories where the research was primarily directed towards solid state problems.

The study of quadrupolar nuclei can provide unique and very valuable information on a variety of physico-chemical and biological systems. For one thing the relaxation of quadrupolar nuclei is in many ways easier to interpret than the relaxation of non-quadrupolar nuclei, since the former is in many cases caused by purely intramolecular interactions modulated by the molecular motion. Studies of quadrupolar relaxation have therefore furnished important information about molecular reorientation and association in liquids and have played - and will certainly play for many years - an important role in testing new theoretical models of molecular motion in liquids.

Another important parameter that may be obtained in studies of quadrupolar nuclei is the quadrupolar splitting of NMR transitions observable in systems where the nuclei are in an anisotropic environment. Here studies of the NMR spectra can provide a quantitative measure of the ordering of the system at a molecular level.

The chemical exchange of a quadrupolar nucleus between two environments characterized by widely different electric field gradients can give information which in many ways is complementary to that obtainable by the "paramagnetic relaxation enhancement" method for ^1H and other non-quadrupolar nuclei.

In the present monograph we have attempted to present a fairly comprehensive account of one set of related quadrupolar nuclei: chlorine (^{35}Cl and ^{37}Cl), bromine (^{79}Br and ^{81}Br) and iodine (^{127}I). While NMR studies of some of these nuclei were performed very early, many applications, especially in biological systems, are of recent origin and have still not reached a wide audience.

For convenience the material has been divided up in different ways. On the one hand we have discussed separately the *different parameters* that characterize the halogen NMR spectra and on the other we have treated separately *halide ions* and *covalent halogen compounds*. Such a sub-division, however, has its limitations - the need for a separate section for studies of the perchlorate ion exemplifies this.

We have included halogen NMR studies on liquids and solutions as well as on liquid crystalline systems. It is indeed advantageous to treat these in the same context since a number of different NMR parameters such as quadrupole relaxation rates and quadrupole splittings have been determined in the same system and are interrelated.

In the beginning of the chapters dealing with specific applications of chlorine, bromine and iodine NMR we have tried to lay out the basic spectroscopic principles involved. Much of this material is applicable to all quadrupolar nuclei.

Certain readers may be primarily interested only in one particular aspect of halogen NMR. In order to facilitate such selective reading some background material has been reiterated in the opening chapters of 2 to 8, thus hopefully increasing the readability at the expense of some overlapping of content.

We have made efforts to cover the literature as completely as possible up to January 1st 1976, but more recent reports have also been included as far as possible.

The writing of this monograph has taken us more time than originally anticipated - presumably not a unique experience. The great benefit for the authors in such a work is to encounter several interesting problems and indeed the writing of this book has stimulated us to both experimental work and theoretical analyses in many aspects of Cl, Br and I NMR. As the reader will find we have included a considerable portion of unpublished work from our laboratory. A prerequisite for this has been the interested and able help from several of our colleagues and co-workers who have carried out experimental investigations, performed calculations and also helped us through theoretical discussions and through a friendly and valuable criticism of the text.

In particular we wish to thank Tom Bull, Dennis Burton, Bill Egan, Hans Gustavsson, Göran Lindblom, Nils-Ola Persson, Pétur Reimarsson and Håkan Wennerström.

The first version of the manuscript was sent to a number of our colleagues who read the text and gave us valuable comments; in particular we wish to thank Profs. H.G. Hertz, P. Laszlo, P. Diehl, K. Schaumburg and M. Zeppezauer whose suggestions led to significant improvements of the manuscript.

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August 1976

B. Lindman S. Forsén

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