

ANNUAL REPORTS ON NMR SPECTROSCOPY

Volume 37

- **Dynamic NMR spectroscopy in inorganic and organometallic chemistry**
- **Solid-state NMR studies of wood and other lignocellulosic materials**
- **NMR structural studies of iron-sulfur proteins**
- **NMR studies of wine chemistry and wine bacteria**
- **Proton phase-sensitive pulsed field gradient double-quantum spectroscopy**



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NMR SPECTROSCOPY

Edited by

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VOLUME 37



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Preface

As in previous volumes of this series, the current one consists of authoritative accounts of the applications of NMR in various areas of molecular science.

Dynamic NMR Spectroscopy in Inorganic and Organometallic Chemistry is admirably covered by K. G. Orrell; A. M. Gil and C. Pascoal Neto provide an interesting account of Solid-state NMR Studies of Wood and other Lignocellulosic Materials; this is followed by a comprehensive report on NMR Structural Studies of Iron-Sulfur Proteins by B. J. Goodfellow and A. L. Macedo; A. Ramos and H. Santos have given a fascinating account of NMR Studies of Wine Chemistry and Wine Bacteria; finally a thorough study of Proton Phase-sensitive Pulsed Field Gradient Double-quantum NMR Spectroscopy is presented by C. Dalvit and J. M. Böhlen.

It has been a great pleasure for me to have the opportunity of working with these reporters and I am very grateful to them for the prompt delivery of their very valuable and interesting contributions. It is also my pleasant duty to extend my thanks to the production staff at Academic Press (London) for their well-established support and cooperation in the production of this series of reports.

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G. A. WEBB
April 1998

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Dynamic NMR Spectroscopy in Inorganic and Organometallic Chemistry

KEITH G. ORRELL

Department of Chemistry, The University of Exeter, UK

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This article reviews the main advances in theory, methodology and chemical applications of NMR applied to internal motions in molecules. The literature coverage is for the period 1992–1997. It is far from exhaustive but includes those papers which describe important advances in dynamic NMR theory and experiments, and those applications of well-established theory where emphasis has been given to quantitative accuracy of rate and activation energy data, or where the dynamic processes are particularly novel. Most chemical applications relate to inorganic and organometallic compounds since such species display the widest range of internal rate processes. The review highlights the particular power of combining both one- and two-dimensional NMR methods and covers both solid-state and solution studies.

1. INTRODUCTION

This review represents an update of a previous review of this field that appeared in Volume 27 of this series.¹ The literature coverage is for the period 1992–1997, during which time the uses of NMR for studying time-dependent

phenomena in molecules have increased greatly. For a review of this timespan the literature chosen for inclusion has had to be tightly selected. Emphasis has been placed on the main advances in theory and methodology of dynamic NMR (DNMR), and to particularly significant chemical applications of the full range of DNMR methods. Most applications are confined to new inorganic and organometallic compounds, since such species display an exceptionally wide range of dynamic processes. The review is far from exhaustive, but it does aim to provide a clear overview of the directions in which DNMR methods are leading and of the diversity of molecular dynamic phenomena that are currently amenable to NMR study.

During the period of this review, a number of books and monographs containing aspects of DNMR have appeared. Of specific mention are the second editions of the books by Friebohn,² Günther,³ and Sanders and Hunter,⁴ each of which contains specific chapters on dynamic studies. A multi-authored monograph, *Dynamics of Solutions and Fluid Mixtures*, edited by Delpuech,⁵ provides comprehensive coverage of the whole range of time-dependent effects on NMR. This book contains useful chapters on time scales in NMR, with respect to both relaxation phenomena and magnetization transfer induced by nuclear site exchanges. Other chapters relevant to this review include discussions of quadrupolar nuclei as probes of solution dynamics and solvent exchange on metal ions. Finally, the reader is referred to the eight-volume *Encyclopedia of Nuclear Magnetic Resonance*,⁶ which contains numerous articles on different aspects of time-dependent phenomena.

2. ONE-DIMENSIONAL METHODS

The accurate study of chemical exchange processes by NMR demands a knowledge of exchange rate constants over as wide a magnitude range as possible. This requires the use of combinations of NMR techniques, since each technique possesses its own optimal time scale. One-dimensional bandshape analysis can be used over slow, intermediate and fast exchange regimes but is most suited to intermediate rates (typically $10\text{--}10^3\text{ s}^{-1}$). Slower exchange rates (typically $0.1\text{--}10\text{ s}^{-1}$) are most accurately measured by magnetization transfer experiments that rely on nuclear spin-lattice relaxation times, T_1 (viz. selective inversion or saturation recovery, Section 2.2) or site exchanges (viz. 2D-EXSY, Section 3.1). Fast dynamic processes (having rates typically $>10^3\text{ s}^{-1}$) can be measured from knowledge of spin-spin relaxation times, T_2 , or T_1 -based molecular correlation times (Section 2.3).

Developments in all these areas will be discussed.

2.1. Developments in bandshape analysis methods

The current theory for calculating dynamic bandshape and magnetization transfer effects has been reviewed by Johnston,⁷ and a DNMR spectral simulation program suitable for use on a PC has been developed.⁸

A new approach to the calculation of NMR bandshapes of exchanging systems, based on computations in the time domain, has been developed by Bain.^{9,10} The approach involves a re-examination of the nuclear spin transition probability, which may be considered to consist of two terms, one corresponding to the share of the initial magnetization that each spin coherence receives at the start of the experiment, and the other corresponding to how much that coherence contributes to the total detected signal. The final signal intensity is the product of these two terms. For a static spectrum these two terms are complex conjugates, so the product is real and represents the standard transition probability. For an exchanging spectrum the product becomes complex, so the time evolution involves both oscillatory and dispersive terms. The dynamic spectrum is still a sum of individual transitions, but the lineshapes are distorted in phase, intensity, position and linewidth by the dynamic process. The NMR signal is a function of time t as given by

$$\text{NMR signal} = (I_x | \exp \{(-i\mathbf{L} - \mathbf{R} - \mathbf{K})t\} | F_x) \quad (1)$$

where $i\mathbf{L} + \mathbf{R} + \mathbf{K}$ is the Liouville matrix. If $\mathbf{U}$ is the matrix with the eigenvectors as columns and $\mathbf{\Lambda}$ is the diagonal matrix with the eigenvalues on the diagonal, Eq. (1) can be written as Eqs. (2) and (3)

$$\text{NMR signal} = (I_x | U^{-1} \exp(-i\mathbf{\Lambda}t) U | F_x) \quad (2)$$

$$= \sum_j (U^{-1} I_x)_j^* (U F_x)_j \exp(i\lambda_j t) \quad (3)$$

where λ_j are the individual eigenvalues of $\mathbf{\Lambda}$.

This theory has been applied to both uncoupled⁹ and coupled¹⁰ two-site exchange. The case of an exchanging AB system is shown (Fig. 1). The approach differs from that of Binsch in that the latter calculates total signal shapes as a function of frequency, whereas this new method presents signals as a sum of absorption and dispersion lines.

Bain¹¹ has also extended the calculation of dynamic NMR spectra of many-spin systems using a sparse matrix methodology as this is computationally much more efficient than the conventional methodology. The Liouville matrix is a sparse matrix in that it invariably contains many zeros. These can be ignored using the sparse matrix time-dependent Chebyshev method. The computational demands of the new method are predicted to scale as $O(2^n)$ as the number of spins n increases, compared to the scale $O(2^{6n})$ of conventional

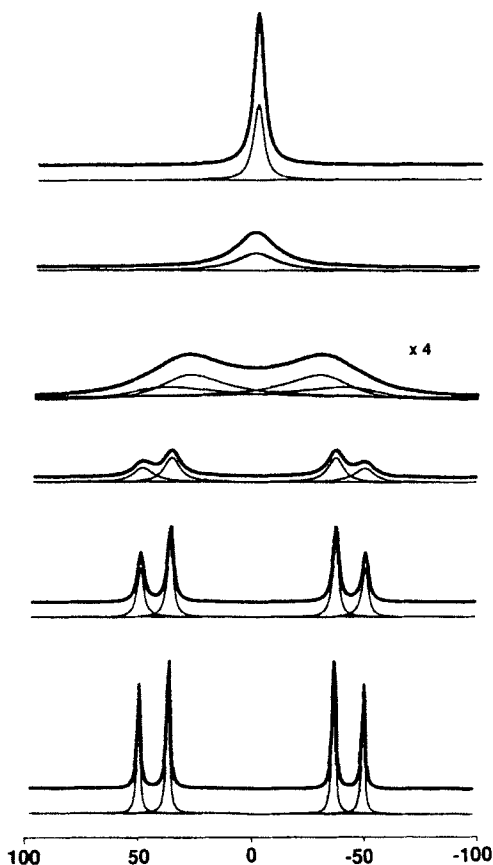


Fig. 1. NMR lineshapes of an AB spin system undergoing mutual exchange. The bold upper line represents the total lineshape and the lighter lines the individual components. The parameters of the spin system are: chemical shift difference 86 Hz, scalar coupling constant 13 Hz, $T_2 = 5$ s for each site. Exchange rates (k/s^{-1}) are 0.1, 5, 25, 125, 625 and 3125. (Reproduced with permission from *Canad. J. Chem.*, 1996, **74**, 819.)

methodology. The method is based on splitting the propagator into Liouville, relaxation and exchange components using Chebyshev expansion of the total exponential function. The author has illustrated the method by simulating the dynamic ^1H spectra of trimethylsilylcyclopenta[*l*]phenanthrene. In this compound the Me_3Si - group migrates from H(1) to H(3) of the 5-membered ring causing mutual exchange of the eight coupled ^1H spins of the phenanthrene ring. Such a simulation could not have been tackled by conventional methodology.

Goldman¹² has developed a new formalism for the analysis of NMR spectra in the presence of exchange that works equally well for all types of exchange-