

Annual reports on
NMR Spectroscopy

Volume 64



Annual Reports on
NMR SPECTROSCOPY

VOLUME **64**

This page intentionally left blank

Annual Reports on **NMR SPECTROSCOPY**

VOLUME **64**

Edited by

GRAHAM A. WEBB

Royal Society of Chemistry

Burlington House

Piccadilly, London, UK



Amsterdam • Boston • Heidelberg • London • New York • Oxford
Paris • San Diego • San Francisco • Singapore • Sydney • Tokyo
Academic Press is an imprint of Elsevier



Academic Press is an imprint of Elsevier
84 Theobald's Road, London WC1X 8RR, UK
Radarweg 29, PO Box 211, 1000 AE Amsterdam, The Netherlands
Linacre House, Jordan Hill, Oxford OX2 8DP, UK
30 Corporate Drive, Suite 400, Burlington, MA 01803, USA
525 B Street, Suite 1900, San Diego, CA 92101-4495, USA

First edition 2008

Copyright © 2008 Elsevier Ltd. All rights reserved

No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means electronic, mechanical, photocopying, recording or otherwise without the prior written permission of the publisher

Permissions may be sought directly from Elsevier's Science & Technology Rights Department in Oxford, UK: phone (+44) (0) 1865 843830; fax (+44) (0) 1865 853333; email: permissions@elsevier.com. Alternatively you can submit your request online by visiting the Elsevier web site at <http://www.elsevier.com/locate/permissions>, and selecting *Obtaining permission to use Elsevier material*

Notice

No responsibility is assumed by the publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein. Because of rapid advances in the medical sciences, in particular, independent verification of diagnoses and drug dosages should be made

ISBN: 978-0-12-374337-4

ISSN: 0066-4103

For information on all Academic Press publications
visit our website at books.elsevier.com

Printed and bound in Great Britain

08 09 10 11 12 10 9 8 7 6 5 4 3 2 1

Working together to grow
libraries in developing countries

www.elsevier.com | www.bookaid.org | www.sabre.org

ELSEVIER

BOOK AID
International

Sabre Foundation

CONTENTS

<i>Contributors</i>	vii
<i>Preface</i>	ix
1. Theoretical and Experimental Studies on ^{19}F NMR Shieldings in Mineral Glasses, Zeolites and Related Silsesquioxanes	1
J.A. Tossell	
1. Introduction	2
2. Recommended Computational Methods	3
3. Fluorine in Aluminosilicate Glasses	5
4. Fluorine in Zeolites (Low-Density, Large-Pore Aluminosilicates) and in Silsesquioxanes	11
5. Al in Hydroxyfluorides: Rosenbergite	16
6. Conclusion	18
Acknowledgment	18
References	18
2. NOE Studies of Solvent–Solute Interactions	21
J.T. Gerig	
1. Introduction	22
2. Methods Used to Examine Solvent–Solute Interactions	24
3. Scope of this Chapter	26
4. Theoretical Background	26
5. Experimental Considerations	36
6. Applications	38
Acknowledgments	69
References	69
3. DFT Computations of Transition-Metal Chemical Shifts	77
Michael Bühl	
1. Introduction	78
2. Methodological Aspects	80
3. 3d-Metals	85
4. 4d-Metals	99
5. 5d-Metals	111
6. Actinides	118
7. Concluding Remarks	118
Abbreviations	119
Acknowledgements	121
References	121

4. Solid-State NMR Studies of Collagen Structure and Dynamics in Isolated Fibrils and in Biological Tissues	127
Daniel Huster	
1. Introduction	128
2. Experimental Methods to Study the Molecular Dynamics in Collagen	132
3. Selected Examples	139
4. Conclusions	155
Acknowledgements	156
References	156
5. NMR Study of Beverages	161
J. Kidrič	
1. Introduction	161
2. Novel Methods for the Analysis of Beverages	162
3. Analysis and Authentication	163
References	169
6. Contribution of NMR Spectroscopy to Flavour Release and Perception	173
L. Tavel, E. Guichard and C. Moreau	
1. Introduction	174
2. NMR Diffusion of Small Solutes	175
3. Aroma–Macromolecule Interactions Using NMR Spectroscopy	183
4. Conclusion	186
References	186
7. Polymer Blend Miscibility	189
Jeffery L. White and Marcin Wachowicz	
1. Introduction	190
2. Recent Developments in Spin-Diffusion and Polymer Blends	191
3. Blends of Polymers that Contain Heteroatoms	196
4. Binary Blends of Polymers Containing Only sp^3 Carbons: Polyolefins	200
5. Blends Containing Vinyl or Diene Polymer Components	203
6. Biopolymer Blends	204
7. Conclusions	206
References	206
Subject Index	211

CONTRIBUTORS

Michael Bühl

Max-Planck Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr, Germany; Present address: School of Chemistry, North Haugh, University of St. Andrews, St. Andrews, Fife, KY16 9ST, UK

J.T. Gerig

Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA 93106, USA

E. Guichard

UMR1129 FLAVIC, ENESAD, INRA, Université de Bourgogne, 17 rue Sully, B.P. 86510, 21065 Dijon, France

Daniel Huster

Institute of Medical Physics and Biophysics, Härtelstr. 16–18, D-04107 Leipzig, Germany

J. Kidrič

National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia

C. Moreau

UMR1129 FLAVIC, ENESAD, INRA, Université de Bourgogne, 17 rue Sully, B.P. 86510, 21065 Dijon, France

L. Tavel

UMR1129 FLAVIC, ENESAD, INRA, Université de Bourgogne, 17 rue Sully, B.P. 86510, 21065 Dijon, France

J.A. Tossell

Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, USA

Marcin Wachowicz

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078

Jeffery L. White

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078

This page intentionally left blank

PREFACE

It is my great pleasure to introduce Volume 64 of Annual Reports on NMR. As is usual with this series of cutting edge reports the great importance of NMR in many areas of scientific research is highlighted.

The volume commences with a chapter on Theoretical and Experimental Studies on ^{19}F NMR Shieldings in Mineral Glasses, Zeolites and Related Silsequioxanes by J.A. Tossell. Chapter 2 is on NOE Studies of Solvent-Solute Interactions by G.T. Gerig. Chapter 3 is a state-of-the-art account of DFT Computations of Transition Metal Chemical Shifts by M. Bühl; this is followed by a contribution from D. Huster on Solid-State NMR Studies of Collagen Structure and Dynamics in Isolated Fibrils and in Biological Tissues; J. Kidrič reports on NMR Studies of Beverages; the Contribution of NMR Spectroscopy to Flavour Release and Perception is covered by L. Tavel, E. Guichard and C. Moreau; the final contribution by J.L. White is on Polymer Blend Miscibility.

My gratitude for their very interesting reports is due to all of these contributors. My thanks also go to the production staff at Elsevier for their help in the timely appearance of volumes of Annual Reports on NMR Spectroscopy.

G.A. Webb
Royal Society of Chemistry
Burlington House
Piccadilly
London, UK

This page intentionally left blank

Theoretical and Experimental Studies on ^{19}F NMR Shieldings in Mineral Glasses, Zeolites and Related Silsesquioxanes

J.A. Tossell

Contents	1. Introduction	2
	2. Recommended Computational Methods	3
	3. Fluorine in Aluminosilicate Glasses	5
	4. Fluorine in Zeolites (Low-Density, Large-Pore Aluminosilicates) and in Silsesquioxanes	11
	5. Al in Hydroxyfluorides: Rosenbergite	16
	6. Conclusion	18
	Acknowledgment	18
	References	18

Abstract

While much attention has been devoted to the measurement and calculation of O NMR shieldings in solid oxides and silicates, F has been seriously neglected. This is because, except for the metal fluorides, F enters most solids as a low-concentration impurity or defect. Yet, the presence of only small amounts of F can exercise enormous influence upon physical properties, such as phase relations and viscosity, and upon chemical reactivity and mechanism of formation. Since the 1990s a number of studies have shown that F NMR shieldings in solids can be calculated quite accurately using quantum methods, which use large flexible basis sets and partially incorporate electron correlation, so long as the cluster model for the solid is adequate. Studies directed toward the assignment of particular unexpected peaks in specific glasses or disordered solids, as well as more general studies of trends in F NMR shifts have both been performed. We now have a good general understanding of the effect of local and mid-range structure about F on its NMR shift. However, for any given site trends often