

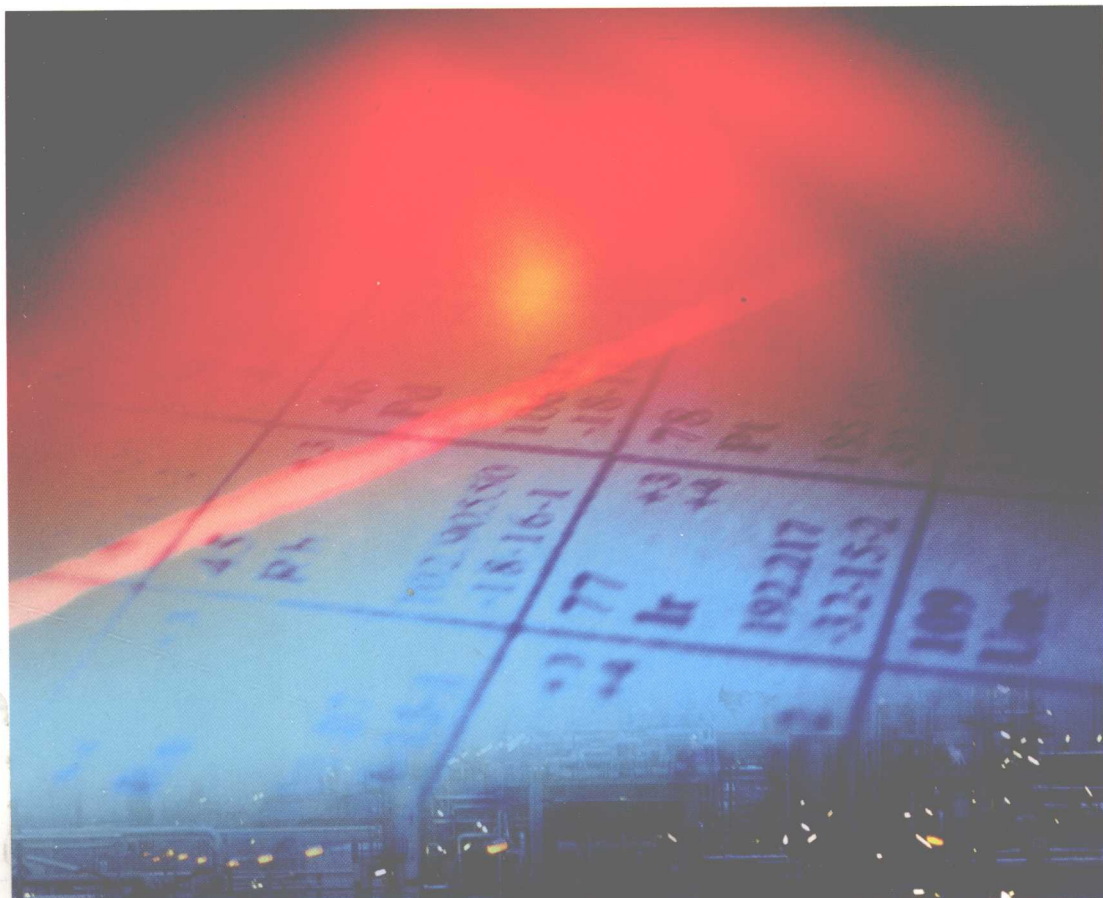
Edited by Maximilian Lackner

 WILEY-VCH

Lasers in Chemistry

Probing Matter

Volume 1





30805486

Lasers in Chemistry

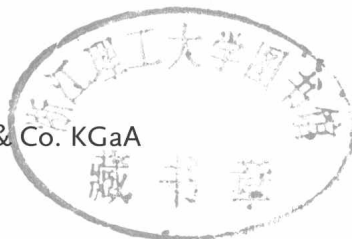
Volume 1

Probing Matter

Edited by
Maximilian Lackner



WILEY-VCH Verlag GmbH & Co. KGaA



The Editor

Dr. Maximilian Lackner

Vienna University of Technology
Institute of Chemical Engineering
Getreidemarkt 9 /166
1060 Wien
Austria

All books published by Wiley-VCH are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Library of Congress Card No.:

applied for

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

**Bibliographic information published by
the Deutsche Nationalbibliothek**

Die Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <<http://dnb.d-nb.de>>.

© 2008 WILEY-VCH Verlag GmbH & Co.
KGaA, Weinheim

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Composition Laserwords Private Limited,
Chennai, India

Printing Betz-Druck GmbH, Darmstadt

Bookbinding Litges & Dopf GmbH,
Heppenheim

Printed in the Federal Republic of Germany
Printed on acid-free paper

ISBN: 978-3-527-31997-8

30805486

Lasers in Chemistry

Edited by
Maximilian Lackner

Volume 1

Further Reading

Lubatschowski, H.

Laser in Medicine

Laser-Tissue Interaction and Applications

2009

ISBN: 978-3-527-40416-2

Misawa, H., Juodkazis, S. (Eds.)

3D Laser Microfabrication

Principles and Applications

2006

ISBN: 978-3-527-31055-5

Schwedt, G.

Analytische Chemie

Grundlagen, Methoden und Praxis

2008

ISBN: 978-3-527-31206-1

Buus, J., Amann, M.-C., Blumenthal, D. J.

Tunable Laser Diodes and Related Optical Sources

2005

ISBN: 978-0-471-20816-7

Schnabel, W.

Polymers and Light

Fundamentals and Technical Applications

2007

ISBN: 978-3-527-31866-7

Meschede, D.

Optics, Light and Lasers

**The Practical Approach to Modern Aspects
of Photonics and Laser Physics**

2007

ISBN: 978-3-527-40628-9



Foreword

Dear Reader,

It is a honor and pleasure for me to give a short perspective to lasers and their applications from the chemical engineering and my personal point of view.

As we do research in the area of energy conversion, fluidized bed combustion and high temperature processes in general we develop new processes and optimize existing ones. To do this in an efficient manner it is of high importance to understand the underlying chemical mechanism and its kinetics. In practice the chemistry is closely related to heat and mass transfer phenomena and depends significantly on the temperature and mixing level of the reaction system. To probe such complex systems, it is not enough to measure the transient behavior of the key species leaving the reaction system. It is very important to obtain time – dependent information from the inside of the system, from *in situ* measurements and not only of stable final products like CO and CO₂ (if you think about combustion) but also from intermediate short-time living species as for example HCN (if you think about fuel NO_x formation) or radicals like OH.

To optimize laboratory – scale systems and to be able to transfer the data to industrial scale units the Concept of Chemical Similarity [1] is used. The concept says that it is important to investigate the chemistry under conditions which are similar to the conditions which occur in the industrial-scale system. The similarity is defined by the so-called similarity criteria. One important similarity criterion is that species' concentrations should be in the same order of magnitude and not only the final stable species but also the intermediate, short-time living species because they also affect significantly the reaction paths.

To understand such complex reaction systems we have developed new and applied existing laser measurement systems and probed our reactors *in situ* [e.g. 2]. We have adopted our reactors with quartz glass windows to allow in-line-of-sight measurements. The information obtained on for example species concentration was very important to test our simulation tools for the ongoing chemical mechanism combined with heat and mass transfer phenomena. These results led to significant improvements and understanding of the underlying chemistry and reduced significantly the risks for scale-up and uncertainties to transfer the results to industrial – scale units.

Another application of such *in situ* measurements is the integration of this early information into control systems of industrial-scale units. With this early information the control system is able to respond significantly faster to changes in optimal conditions [3], for example to reduce pollutants.

As we, as chemical engineers, continued to work with lasers we used lasers not only to probe the systems to get a better understanding of the reaction mechanism we also used lasers to start our reaction systems, for example to ignite fuel-air systems under engine conditions [4] or solid reaction systems for automotive safety [5] as they can be found in airbags. We also used lasers for the cleaning of our combustion windows even under engine conditions [6]. Recently, we also applied lasers to simulate the high heat transfer rates to plastic particles as they occur in blast furnaces [7].

As we learned more and more about lasers we realized what a versatile tool they can be. Applications not only in chemical engineering and chemistry but also in medicine and biology are already daily life. Furthermore, a significant increase of laser applications can be expected in future because the possible potentials are not used by far and the development of new, robust and cost-effective laser systems is increasingly ongoing.

Such a wide range of development and application is only possible by doing research work jointly. Therefore I highly recommend to exchange knowledge and start further cooperations in the area of laser development and application. I think these books are a wonderful basis and may contribute to start and link a network of expertise.

Finally, I also want to give my sincere thanks to my colleague and dear friend Dr Maximilian Lackner who initiated and carried out *Lasers in Chemistry* for all his enthusiasm and encouragement.

Franz Winter
Professor of Chemical Engineering
Vienna University of Technology

References

- 1 Winter, F. (2000) *The concept of chemical similarity for optimization and design of gas-solid processes*, Habilitation – Thesis, Vienna University of Technology, Vienna, Austria.
- 2 Lackner, M., Totschnig, G., Löffler, G., Hofbauer, H. and Winter, F. (2004) “Carbon conversion of solid fuels in the freeboard of a laboratory-scale fluidized Bed combustor (FBC) – application of in-situ laser spectroscopy”. *Fuel*, **83**, 1289–98.
- 3 Schwarzott, M., Lackner, M., Winter, F. and Klausner, J. (2005) *Probemessung Mittels Neuartigem Laser-Messsystems in der Biogasanlage Rohkraft.net/Reidling (Test Measurements of a Novel Laser System in the Biogas Unit Rohkraft.net/Reidling)*, August 2005, <http://www.rohkraft.net>.
- 4 Lackner, M., Winter, F., Graf, J., Geringer, B., Weinrotter, M., Kopecek, H., Wintner, E., Klausner, J. and Herdin, G. (2004) “*Laser Ignition in Internal Combustion Engines –*

- A Contribution to a Sustainable Environment'*. Proceedings of 14th IFRF Members' Conference, International Flame Research Foundation (IFRF), May 11–14, 2004, Noordwijkerhout, The Netherlands.
- 5 Lackner, M. and Winter, F. (2006) *Laser Ignition of Solid Explosives for Automotive Applications*. Poster Presented at Combura 2006, October 6, Dutch Section of the Combustion Institute (V. Meerveld), Nieuwegein, Netherlands.
 - 6 Ranner, H., Tewari, P.K., Kofler, H., Lackner, M., Wintner, E., Agarwal, A.K. and Winter, F. (2007) "Laser cleaning of optical windows in internal combustion engines". *Optical Engineering*, **46**, 104301.
 - 7 Lackner, M., Schwarzott, M., Liedl, G. and Winter, F. (2007) "Heat Transfer to a Single Plastic Resin Particle – Experimental Investigations by Flames and Laser Pulses". Proceedings of 3rd European Combustion Meeting (ECM), April 11–13, 2007, Crete, Greece.

Preface

Laser technology has shown a remarkably fast evolution. Lasers have found numerous applications in virtually all fields of science and engineering, harnessing the unique properties of laser light. Among these are monochromaticity, coherence, collimation and high power. In chemistry, they are also deployed in various ways, thereby improving traditional techniques or even making new ones possible.

This book is an attempt to draw a bow across the wide and exciting topic of lasers in chemistry. More than 50 authors, all renowned experts in their fields, have contributed to this work.

There is a balance between authors from academia and authors from industry.

Text books that cover the subject of 'Lasers in Chemistry' are [1–4]. Early review articles can be found in [5–7]. Several conferences have also covered the topic in its breadth, one of the first events being the Conference on Lasers in Chemistry organized by the Royal Institution, London, in 1977. The laser was soon recognized as a bright, coherent and high-resolution light source with many promising properties. However, its penetration into chemists' labs has been a comparatively slow process. The proliferation in commercial, analytical instruments is even less as discussed in [8].

This book is organized as follows: There are two volumes.

Volume 1 contains an introduction to the principles of lasers and some considerations on laser safety. Laser safety is vital and must always be kept in mind.

The focus of volume 1 is the use of lasers as probes. Various techniques are described where the laser is used to gain information on the system under investigation. The techniques can coarsely be distinguished into those based on absorption, emission and scattering. Some techniques are used for sampling or sample preparation.

Volume 2 deals with the use of lasers to start and influence chemical reactions. Among the topics are laser ignition, laser-based nano-particle formation and photochemical reactions. This volume also covers the use of lasers in neighbouring disciplines such as material processing, biology and medicine. The final chapters in volume 2 present the historic development and some trends on laser research and development. Outlook and glossary conclude the book.

The book strives to serve different purposes:

With its scope of over 50 Chapters and the contributions of high profile authors, the book can be seen as a reference on the topic of 'Lasers in Chemistry'.

Up to date, except for conference proceedings, no similar book has been brought on the market to cover the topic in its breadth.

Thereby, the book documents the state of the art in research and development of lasers in chemistry and their use in chemical production plants. It summarizes the achievements obtained so far.

The chapters are designed in a way that they give a brief introduction to the respective topic to get new readers started, similarly to a review article.

Probably the biggest benefit will stem from stimulating new thought and ideas; Several important technologies are the outcome of a combination of existing techniques. Examples for such an outcome are hyphenated analytical methods like GC/MS. The reader of the book, being an expert in one of the fields, might discover an interesting aspect in another discipline and try to apply knowledge from there to his own work.

This cross-fertilisation might lead to totally new analytics or synthesis methods, process control applications or novel materials. Experts in various fields, though concerned with similar challenges, tend to speak a language of their own with special terms, such as 'degrees crank angle' as a substitute for time amongst engine researchers and 'wave numbers' instead of wavelength amongst spectroscopists. If this book can create some common understanding and stimulate thoughts, it has achieved its objectives.

Highlights of the respective chapters, of which there are several, are outlined in Chapter 3 for the area of lasers as probes and in Chapter 24 for lasers as reaction starters.

The authors wish the readers many fruitful insights, as they embark on a fascinating journey on 'Lasers in Chemistry'.

Maximilian Lackner
Institute of Chemical Engineering
Vienna University of Technology

References

- 1 Kompa, K.L. and Wanner, J. (eds) (1982) "*Laser Applications in Chemistry*". NATO ASI Series, Series B: Physics", in Proceedings of the NATO Advanced Study Institute on Laser Applications to Chemistry, ISBN 0-306-41622-0, Vol. 105, June 27–July 11, San Minato, Italy.
- 2 Jackson, W.M. and Harvey, A.B. (eds) (1985) *Lasers as Reactants and Probes in Chemistry*, ISBN 0-88258-141-4, Howard University Press, Washington, DC.
- 3 Steinfeld, J.I. (ed) (1981) *Laser-induced Chemical Processes*, Plenum Press, New York, London.
- 4 Van Hecke, G.R. and Karukstis, K.K. (1998) *A Guide to Lasers in Chemistry*, ISBN 0-7637-0412-1, Jones and Bartlett Publishers.

- 5 Lockhart, L.B. (1974) "Lasers in chemistry". *Optics and Laser Technology*, **6** (4), 159–65.
- 6 Müller, A. (1990) "Laser in der chemie". *Chemie in Unserer Zeit*, **24** (6), 280–91.
- 7 Kleinermanns, K. and Wolfrum, J. (1987) "Laser in der chemie – wo stehen wir heute? (Laser chemistry – what is its current status?)" *Angewandte Chemie*, **99**, 38–58.
- 8 Smith, B. (2007) "25 years of lasers and analytical chemistry: a reluctant pairing with a promising future". *TrAC Trends in Analytical Chemistry*, **26** (1), 60–64.

List of Contributors

Heidi Abrahamse

University of Johannesburg
Faculty of Health Sciences
Laser Research Group
PO Box 17011, Doornfontein
Johannesburg
South Africa

Xavier Allonas

University of Haute Alsace
Department of Photochemistry
3, rue Alfred Werner
68093 Mulhouse
France

Freek Ariese

Vrije Universiteit Amsterdam
Laser Centre
De Boclelaan 1083
1081 HV Amsterdam
The Netherlands

John F. Asmus

University of California, San Diego
Institute for Pure and Applied Physical
Sciences
9500 Gilman Dr.
La Jolla, CA 92093-0360
USA

Parma Nand Bajaj

Bhabha Atomic Research Centre
Radiation and Photochemistry Division
Trombay, Mumbai
India, 400 085

Franziska Beer

Vienna Medical University
Dental school
Währinger Strasse 25A
1090 Vienna
Austria

Thorsten Benter

University of Wuppertal
Department of Chemistry
Gaußstraße 20
42119 Wuppertal
Germany

Khalid Bougrin

Faculté des Sciences
Département de Chimie
Laboratoire de Chimie des Plantes et de
Synthèse Organique et Bioorganique
BP 1014 Rabat
Morocco

Andres D. Campiglia

University of Central Florida
Department of Chemistry
P.O. Box 162366
Orlando, FL 32816-2366
USA

Svatopluk Civiš

Academy of Sciences of the Czech Republic
J. Heyrovský Institute of Physical Chemistry
Dolejškova 3
182 21 Prague 8
Czech Republic

Frances L. Cozens

Dalhousie University
Department of Chemistry
Halifax, Nova Scotia
B3H 4J3
Canada

Céline Croutxe-Barghorn

University of Haute Alsace
Department of Photochemistry
3, rue Alfred Werner
68093 Mulhouse
France

Francesco D'Amato

Consiglio Nazionale delle Ricerche
National Institute of Applied Optics
Largo E. Fermi 6
50125 Firenze
Italy

Joost S. de Klerk

Vrije Universiteit Amsterdam
Laser Centre
De Boelelaan 1083
1081 HV Amsterdam
The Netherlands

El Houssaine El Rhaleb

Faculté des Sciences
Département de Physique
Laboratoire de Spectrométrie Moléculaire
Optique et Instrumentation Laser
BP 1014 Rabat
Morocco

Pavel Engst

LIDAR, s.r.o.
Washingtonova 17
110 00 Prague 1
Czech Republic

Hans-Jochen Foth

University of Kaiserslautern
Department of Physics
Erwin-Schrödinger-Straße
67663 Kaiserslautern
Germany

Jean-Pierre Fouassier

University of Haute Alsace
Department of Photochemistry
3, rue Alfred Werner
68093 Mulhouse
France

Heribert Fuchs

AVL
List GmbH
Hans-List-Platz 1
8020 Graz
Austria

Yann A. Gauduel

Ecole Polytechnique – ENS Techniques
Avancées, LOA-CNRS UMR 7639
Chemin de la Hunière
91761 Palaiseau
France

Gerhard Geipel

Forschungszentrum Dresden-Rossendorf
 Institute of Radiochemistry
 P.O. Box 510119
 01324 Dresden
 Germany

Hossein Golnabi

Sharif University of Technology
 Institute of Water and Energy
 PO Box 11365-8639
 Teheran
 Iran

Mohammed Ashraf Gondal

King Fahd University of Petroleum
 and Minerals
 Department of Physics
 Box 5047
 Dhahran 31261
 Saudi Arabia

Leticia González

Friedrich-Schiller-Universität Jena
 Institut für Physikalische Chemie
 Helmholtzweg 4
 07743 Jena
 Germany

Cees Gooijer

Laser Centre
 Vrije Universiteit Amsterdam
 De Boelelaan 1083
 1081 HV Amsterdam
 The Netherlands

Debabrata Goswami

Indian Institute of Technology
 Department of Chemistry
 Kanpur
 Uttar Pradesh 208016
 India

Michael R. Hamblin

Harvard-MIT Division of
 Health Sciences and Technology
 77 Massachusetts Avenue
 Cambridge, MA 02139
 USA

and

Massachusetts General Hospital
 Wellman Center for Photomedicine
 40 Blossom Street
 Boston, MA 02114
 USA

and

Harvard Medical School
 Department of Dermatology
 55 Fruit Street
 Boston, MA 02114
 USA

Norbert Hampp

University of Marburg
 Department of Chemistry
 Hans-Meerwein-Straße
 35032 Marburg
 Germany

and

Material Science Center Marburg
 Hans-Meerwein-Straße
 35032 Marburg
 Germany

Johan Hult

University of Cambridge
 Department of Chemical Engineering
 Pembroke Street
 Cambridge CB2 3RA
 UK

Libor Juha

Academy of Sciences of the Czech Republic
Institute of Physics
Na Slovance 2
182 21 Prague 8
Czech Republic

Hee-Cheol Kim

University of Marburg
Department of Chemistry
Hans-Meerwein-Straße
35032 Marburg
Germany

Seong-Soo Kim

Georgia Institute of Technology
School of Chemistry and Biochemistry
901 Atlantic Drive
Atlanta, GA 30067
USA

Nikolai A. Kirichenko

A.M. Prokhorov
General Physics Institute
RAS (Russian Academy of Science)
38, Wave Research Center
Vavilov Street
119991 Moscow
Russia

Heinrich Kofler

Vienna University of Technology
Photonics Institute
Gusshausstrasse 27-29
1040 Wien
Austria

Awadhesh Kumar

Bhabha Atomic Research Centre
Radiation and Photochemistry Division
Trombay, Mumbai
India, 400 085

Maximilian Lackner

Institute of Chemical Engineering
Vienna University of Technology
Getreidemarkt 9/166
1060 Wien
Austria

Jacques Lalevée

University of Haute Alsace
Department of Photochemistry
3, rue Alfred Werner
68093 Mulhouse
France

Soo-Keun Lee

Daegu Gyeongbuk Institute of Science
and Technology
BioConvergence Technology Research Team
5th Floor, Daegu Techno-park, Venture 2
711 Hosan-dong, Dalseo-gu
704-230 Daegu
Korea

Gerhard Liedl

Vienna University of Technology
Institute for Forming- and High-power Laser
Technology
Franz-Grill-Strasse 1
1030 Wien
Austria

Milton S.F. Lima

Institute for Advanced Researches (IEAv)
CP 6044
12228-970 Sao Jose dos Campos (SP)
Brazil

Jean-Pierre Malval

University of Haute Alsace
Department of Photochemistry
3, rue Alfred Werner
68093 Mulhouse
France

Michael Markus

Siemens AG Industry
 Industry Automation
 I IA SC PA PM
 Östl. Rheinbrückenstrasse 50
 76187 Karlsruhe
 Germany

Boris Mizaikoff

University of Ulm
 Institute of Analytical and Bioanalytical
 Chemistry
 Albert-Einstein-Allee 11
 89081 Ulm
 Germany

Fabrice Morlet-Savary

University of Haute Alsace
 Department of Photochemistry
 3, rue Alfred Werner
 68093 Mulhouse
 France

Alexander Morozov

AVL
 List GmbH
 Hans-List-Platz 1
 8020 Graz
 Austria

Pawel Mroz

Massachusetts General Hospital
 Wellman Center for Photomedicine
 40 Blossom Street
 Boston, MA 02114
 USA

and

Harvard Medical School
 Department of Dermatology
 55 Fruit Street
 Boston, MA 02114
 USA

Maurizio Musso

University of Salzburg
 Department of Materials Engineering
 and Physics
 Hellbrunnerstrasse 34
 5020 Salzburg
 Austria

Abbey G. Myers

Kigre, Inc.
 100 Marshland Road
 Hilton Head Island, SC 29926
 USA

John D. Myers

Kigre, Inc.
 100 Marshland Road
 Hilton Head Island, SC 29926
 USA

Michael J. Myers

Kigre, Inc.
 100 Marshland Road
 Hilton Head Island, SC 29926
 USA

Prakash D. Naik

Bhabha Atomic Research Centre
 Radiation and Photochemistry Division
 Trombay, Mumbai
 India, 400 085

Karl-Ludwig Oehme

Friedrich-Schiller-University Jena
 Institute of Physical Chemistry
 Lessingstrasse 10
 07743 Jena
 Germany

Tatsuo Okada

Systems Engineering
 Department of Electrical and Electronic
 Kyushu University
 Moto-OKA 744, Fukuoka 819-0395
 Japan

Venkatachari Parthasarathy

Bhabha Atomic Research Centre
Laser and Plasma Technology Division
Trombay, Mumbai
India, 400 085

Peter K. J. Robertson

The Robert Gordon University
Centre for Research in Energy
and the Environment
Schoolhill
AB10 1FR
Aberdeen
UK

Friedrich Röhrbacher

Austrian Research Centers GmbH-ARC
Radiation Safety and Applications
2444 Seibersdor
Austria

Bodo Ruck

University of Karlsruhe
Laboratory of Building- and
Environmental Aerodynamics/
Institute for Hydromechanics
Kaiserstrasse 12
76128 Karlsruhe
Germany

Douglas K. Russell

University of Auckland
Department of Chemistry
Private Bag 92019
Auckland 1142
New Zealand

Janusz Ryczkowski

University of Maria Curie-Skłodowska
Department of Chemical Technology
Faculty of Chemistry
Pl. M. Curie-Skłodowskiej 3
20-031 Lublin
Poland

Sisir Kumar Sarkar

Bhabha Atomic Research Centre
Radiation and Photochemistry Division
Trombay, Mumbai
India, 400 085

Sascha Sauer

Max Planck Institute for Molecular Genetics
Otto-Warburg-Laboratory
Innestrasse 63-73
14195 Berlin
Germany

Norman P. Schepp

Dalhousie University
Department of Chemistry
Halifax, Nova Scotia
B3H 4J3
Canada

Oliver J. Schmitz

University of Wuppertal
Department of Chemistry
Gaußstraße 20
42119 Wuppertal
Germany

Martin Schraub

University of Marburg
Department of Chemistry
Hans-Meerwein-Straße
35032 Marburg
Germany

G.A. Shafeev

A. M. Prokhorov General Physics Institute
Russian Academy of Sciences
Wave Research Centre
38, Vavilov street
119991 Moscow
Russia