IMAGING IN MOLECULAR DYNAMICS

Charged particle imaging has revolutionized experimental studies of photodissociation and bimolecular collisions. Written in a tutorial style by some of the key practitioners in the field, this book gives a comprehensive account of the technique and describes many of its recent applications.

The book is split into two parts. Part I is intended as a series of tutorials. It explains the basic principles of the experiment and the numerical methods involved in interpreting experimental data. After an historical introduction, this section contains a discussion of the basic experiment and goes on to review image reconstruction techniques. The final chapters discuss alternative approaches to charged particle imaging and explore the possibility of employing the technique in conjunction with femtosecond pump-probe methods to study the excited state dynamics of molecules.

Part II describes a number of different applications. These chapters are more directly research oriented, the aim being to introduce the reader to the possibilities for future experiments. The first chapter describes the power of coincidence imaging detection. The possibilities for probing bimolecular collisions are explored in the following chapters and the final chapter introduces a new approach to ion imaging and velocity mapping called slice imaging.

This comprehensive book will be of primary interest to researchers and graduate students working in chemical and molecular physics who require an overview of the subject as well as ideas for future experiments.

BEN WHITAKER graduated from Sussex University with first class honours in Chemical Physics in 1978 and a D.Phil. three years later with a thesis on state-to-state rotational energy transfer using high-resolution laser spectroscopy under the supervision of Prof. Tony McCaffery. He subsequently worked briefly at the Université de Provence, Marseilles and then at the Université de Paris-Sud where he developed, together with Prof. Philippe Bréchignac, the AON model for rotational energy transfer between small molecules that emphasized the role of angular momentum constraints. In 1983 he returned to Sussex where he continued to work on energy transfer and laser polarization spectroscopy and, with Prof. Tony Stace, on cluster spectroscopy. In 1988 he left Sussex to work with Prof. Paul Houston at Cornell University where he began work on ion imaging. A year later he took up his present position as a Lecturer, and then Reader at Leeds University. He is the author of some seventy papers mainly in the field of molecular reaction dynamics, but his research interests also span a number of areas from computer to combustion science. In his spare time he enjoys making and flying kites, walking in the Yorkshire Dales and the occasional pint of Taylor's Landlord (or Harvey's Best if he is in Sussex). Most of all he enjoys talking science with friends and colleagues, many of whom have contributed to this volume.

IMAGING IN MOLECULAR DYNAMICS

Technology and Applications
(A User's Guide)

Edited by BENJAMIN J. WHITAKER
Department of Chemistry, University of Leeds, Leeds, UK

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Contributors

David W. Chandler
Combustion Research Facility, Sandia National Laboratories, Livermore, California, USA.

Alexei I. Chichinin
Institute of Chemical Kinetics and Combustion, 630090, Novosibirsk, Russia.

Tina S. Einfeld
Institut für Physikalische und Theoretische Chemie, Technische Universität Braunschweig, Hans-Sommer-Str. 10, D38106 Braunschweig, Germany.

André T. J. B. Eppink
Department of Molecular and Laser Physics, University of Nijmegen, Toerooiveld 11, 6525 ED, Nijmegen, The Netherlands.

Karl-Heinz Gericke
Institut für Physikalische und Theoretische Chemie, Technische Universität Braunschweig, Hans-Sommer-Str. 10, D38106 Braunschweig, Germany.

Oded Heber
Department of Particle Physics, Weizmann Institute of Science, Rehovot, 76100, Israel.

Hanspeter Helm
Universität Freiburg, Fakultät für Physik. Hermann-Herder-Str. 3, D-79104, Freiburg, Germany.

Paul L. Houston
Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York, USA.

Theofanis N. Kitsopoulos
Department of Chemistry, University of Crete, 71409, Heraklion, and Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas (IESL-FORTH), 711 10 Heraklion, Crete, Greece.

K. Thomas Lorenz
Lawrence Livermore National Laboratory, Livermore, California. USA.

Christof Maul
Institut für Physikalische und Theoretische Chemie, Technische Universität Braunschweig, Hans-Sommer-Str. 10, D38106 Braunschweig, Germany.

Ulrich Müller
Universität Freiburg, Fakultät für Physik Hermann-Herder-Str. 3, D-79104, Freiburg, Germany.

David H. Parker
Department of Molecular and Laser Physics, University of Nijmegen, Toerooiveld 11, 6525 ED, Nijmegen, The Netherlands.

T. Peter Rakitzis
Department of Physics, University of Crete, 710 03 Heraklion, and Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas (IESL-FORTH), 711 10 Heraklion, Crete, Greece.

James L. Springfield
Griffith University, Brisbane, Australia.

Daniel Strasser
Department of Particle Physics, Weizmann Institute of Science, Rehovot, 76100, Israel.

Toshinori Suzuki
Graduate Chemical Dynamics Laboratory, RIKEN, Wako 351-0198, Japan and PRESTO, Japan Science and Technology Corporation, Japan.

Elisabeth A. Wade
Combustion Research Facility, Sandia National Laboratories, Livermore, California, USA. (Current address: Department of Chemistry and Physics, Mills College, Oakland, California, USA.)

Benjamin J. Whitaker
Department of Chemistry, University of Leeds, Leeds LS2 9JT, UK.

Shio-Min Wu
Department of Molecular and Laser Physics, University of Nijmegen, Toerooiveld 11, 6525 ED, Nijmegen, The Netherlands.

Daniel Zajfman
Department of Particle Physics, Weizmann Institute of Science, Rehovot, 76100, Israel.

Preface and acknowledgements

The field of molecular reaction dynamics has made enormous progress since the pioneering experiments of Yuan Lee, Dudley Herschbach and John Polanyi. The intervening years have seen numerous developments in both experimental techniques and theoretical methods. For the authors of this book one of the most exciting of these advances was the introduction of charged particle imaging by Dave Chandler and Paul Houston described in their 1987 paper 'Two-dimensional imaging of state-selected photodissociation products detected by multiphoton ionization' published in the *Journal of Chemical Physics*.

I was extremely fortunate to be able to join Paul Houston in Ithaca in 1988/89 where we constructed the second imaging machine (Dave Chandler's original machine in Sandia having been temporarily put out of action in an unfortunate accident that Paul describes in the first chapter). It was an extraordinarily exciting experience to be involved in those earlier experiments and I am extremely grateful to Paul for the opportunity. The early data showed the power of the technique to provide graphic insight into chemical mechanism but it was difficult to obtain quantitative information because of instrumental problems to do with the arrangement of the ion optics. These were overcome by André Eppink and Dave Parker working in Nijmegen. Their 1997 paper 'Velocity map imaging of ions and electrons using electrostatic lenses: application in photoelectron and photofragment ion imaging of molecular oxygen', which appeared in the *Review of Scientific Instruments*, revolutionized the field and saw a step change in the both the quality of the data that could be obtained and the dynamical insight the experiment could provide. Following the publication of their paper the community of 'imagers' has burgeoned around the world. The advance, described in detail in Chapter 2, was to remove the thin wire meshes in the ion extraction optics that we had all previously striven so hard to get smooth and flat. The problem with using grids to extract the charged particles, however, was that they distorted the trajectories of particles that passed close to the wires and there was a residual image of the grid in the final image, which limited the resolution. In an attempt to overcome this André and Dave designed a new extraction region with many electrodes but still ending in a grid. There is a story that Dave accidentally put his thumb through the grid and that André carried on taking data while the new mesh was on order and so discovered velocity map imaging. The moral being that sometimes it is OK to let your thesis supervisor fiddle with your experiments! The real story was more prosaic; that while waiting for the workshop to get the job done of producing more electrodes, André started with the two open extraction electrodes ('lens') in combination with the repeller plate, but this only goes to show that it's always a good idea to carry on experimenting even when you think things may not be working perfectly.

And so you see also that this book is aimed at students (of all ages) who want to get involved in imaging experiments and do them for themselves. What we have aimed to do is create a 'users guide' to charged particle imaging that not only describes the kind of information that these experiments are capable of revealing but also gives the 'tricks of the trade'. The first part of the book is intended as a series of tutorials. After an historical introduction, in Chapter 2 we describe the basic experiment and the velocity mapping technique in some detail. In Chapter 3 we review the image reconstruction techniques that are used to extract dynamical information from the recorded images. Chapter 4 extends this discussion to cases where the original data is not cylindrically symmetric. Chapter 5 presents an alternative approach to charged particle imaging in which the ratio of intensities in a pair of 2-D images is used to extract timing information. In the process the chapter also reviews recent developments in camera technology and other charged particle imaging detectors. Chapter 6 introduces the idea of being able to use these developments in detector technology to directly record 3-D velocity distributions without the need for the reconstruction algorithms. In Chapter 7 we explore the possibilities of employing charged particle imaging techniques in conjunction with femtosecond pump-probe techniques to probe in particular the excited state dynamics of molecules.

The second half of the book describes a number of applications. These chapters are more directly research orientated, the aim being to introduce you to the possibilities for future experiments and the understanding of molecular dynamics that they will engender. In Chapter 8 the power of coincidence imaging detection is described. In Chapters 9 and 10 the possibilities for probing bimolecular collisions are explored, while Chapter 11 introduces a new approach to ion imaging and velocity mapping called slice imaging.

The idea for the book grew out of the last meeting of the European Funded IMAGINE TMR (training and mobility of researchers) network (ERB 4061 PL 97–0264) that was held at Fodele on Crete, 21–25 October 2000. Incidentally, Fodele is reputed to have been the birthplace of the sixteenth century painter Domenikos

1. Mike Ashfold; 2. Theofanis Kitsopoulos; 3. Thomas Berg; 4. Ben Whitaker; 5. Wim van der Zande; 6. Dave Parker; 7. Peter Andresen; 8. Dave Chandler; 9. Bob Continetti; 10. Toshi Suzuki; 11. Marc Vrakking; 12. Bernd Witzel; 13. Laura Dinu; 14. Ralph Delmdahl; 15. Celine Nicole; 16. Britta Niederjohann; 17. Hanna Reisler; 18. Daniel Strasser; 19. Albert Stolow; 20. Andrew Orr-Ewing; 21. Maurice Janssen; 22. Bernard Bakker; 23. Wolfgang Roth; 24. Hans-Peter Loock; 25. Javier Aoiz; 26. Yan Picard; 27. Danielle Dowek; 28. Dan Neumark; 29. Marco Beckert; 30. Peter Samartzis; 31. Benoit Soep; 32. Hanspeter Helm; 33. Tim Softley; 34. Eloy Wouters; 35. Eckart Wrede; 36. Rolf Bobbenkamp; 37. Steven Stolte; 38. Karl-Heinz Gericke.

Theotocopoulos, otherwise known as El Greco, and whose curious astigmatic perspective is perhaps a fitting backdrop for a book about imaging. Producing a tutorial guide to imaging seemed a good idea at the time (perhaps influenced by the Blue Lagoon and other cocktails served in the bar in the evenings) but it has taken rather longer than anticipated to bring the project to a conclusion.

We (the authors) are grateful to the European Union for their support, either directly as participants in the IMAGINE programme, or through their support of the international network meeting, which allowed us to share the results of the programme with a wider audience. All of the participants at the meeting (see photograph) have contributed to this book, either as authors or through the many discussions we have all shared. The senior scientists involved in IMAGINE were Peter Andresen (Bielefeld), Mike Ashfold (Bristol), Thomas Berg (La Vision, GmbH), Eran Elizur (El-Mul Technologies, Ltd), Theofanis Kitsopoulos (FORTH, Heraklion), Jon Howorth (Photek plc), David Parker (Nijmegen), Isaac Shariv (El-Mul Technologies, Ltd), Wim van der Zande (AMOLF, Amsterdam), and myself, but the real work was done by the young and very talented postgraduate and postdoctoral scientists employed from across the European Union in the various participating laboratories. These were Richard Thomas, Yan Picard, André Eppink, Eckart Wrede, Eloy Wouters, Bernd Witzel, Derek Smith, Bernard Bakker, Christoph Gebhardt, Pablo Quintata, Wolfgang Roth, Hans-Peter Loock, and Ralph Delmdahl. IMAGINE stood for Imaging Network for the Direct Visualisation of Chemical Dynamics. Its inspiration was Lennonesque, and it was the epitome of the European Union's vision for scientific innovation across the member states. Those of us who were involved with it are extremely grateful for the opportunity it offered us to share our ideas and excitement about the potential of imaging methods in chemical dynamics, and the authors hope that this contribution will sow the same seeds of excitement in a new generation of scientists.

All of us would like to dedicate the volume to the memory of Peter Andresen, who very sadly died suddenly soon after. Peter made enormous contribution to molecular dynamics over the years. His experiments on the photodissociation of water were inspirational, and his enthusiasm for 'imaging', from ions to the insides of motor engines, infectious. He is greatly missed.

Abbreviations

ADC	analogue-to-digital convertor
BBO	beta barium borate
CCD	charge coupled device
CFD	constant fraction discriminator
DCS	differential cross-section
DLD	delay-line detector
DPA	differential pre-amplifier
ESDIAD	electron stimulated desorption ion angular distributions
FFT	fast Fourier transform
FTS	frame threshold suppessor
FWHM	full width half maximum
IC	internal conversion
ISC	intersystem crossing
IVR	intramolecular vibrational energy redistribution
KER	kinetic energy release
LIF	laser-induced fluorescence
MCP	micro-channel plate
MF	molecular frame
MSP	micro-sphere plate
OPA	optical parametric amplifier
OPO	optical parametric oscillator
PAD	photoelectron angular distribution
PES	potential energy surface
PR	pulse router
PSA	position sensitive anode
PSD	position sensitive detector
REMPI	resonance enhanced multiphoton ionization

SE	shaping element
TAC	time-to-analogue converter
TDC	time-to-digital converter
TOF	time-of-flight
TOF-MS	time-of-flight mass spectrometry