Atomic and Molecular Beams
Cover Picture:

(\textit{frontcover, top}) Femtosecond dynamics of the charge-transfer reaction of Benzene (Bz) with Iodine (I-I), a century-old reaction now clarified thanks to Femtochemistry. Shown are the snapshots at different reaction times: 0 fs, 200 fs, and 1500 fs, from the transition state* prepared at the initial femtosecond pulse, to the secondary Bz-I dissociation, as described in the article. Bz + I \rightarrow (Bz^+ 
\rightarrow Bz \cdot I + I \rightarrow Bz + I + I. (From: A.H. Zewail with courtesy of D. Zhong, see also Article 1.1)

(\textit{frontcover, bottom left}) Image of a Bose-Einstein condensate of Rubidium 87 atoms, containing 1 million atoms, released from a magnetic trap. The false color code reveals the atomic density from white (highest density) to dark (lowest density). The elliptical structure at the center (200 \times 100 micrometers) corresponds to what is properly referred to as the ‘condensate’ and the surrounding circular feature represents the non-condensed atoms, at a temperature of the order of 0.3 microkelvin. (From: C. Cohen-Tannoudji with courtesy of P. Desbiolles, D. Guéry-Odelin, J. Soeding, and J. Dalibard, see also Article 1.1)

(\textit{frontcover, bottom right}) Photograph of a corona discharge supersonic free-jet used to generate a beam of metastable nitrogen molecules for the growth of nitride semiconductors. A 1 inch long conical graphite skimmer extracts the isentropic core of the expansion used in supersonic beam epitaxy. (From: R.B. Doak with courtesy of D.C. Jordan, see also Article VII.8)

(\textit{back cover}) Schematic impression of a molecular beam (green) traversing a hexapole quantum state-selector. The state-selected parent molecules are dissociated by a laser pulse (blue) and the neutral fragments are quantum state-selectively ionized by a second laser pulse (red). The three-dimensional recoil distribution of photofragments (CD₃ in this case) are detected by a position sensitive detector located at the end of a time-of-flight tube. (From: M.H.M. Janssen with courtesy of A. van den Brom and M. Janssen, see also Article III.1)
Preface

This book is published about 90 years after the first atomic beam experiment (Dunoyer, 1911). This effusive beam technique has been used for over half a century in many historical beam experiments to establish the basic principles of Modern Physics. Such accomplishments have been celebrated by Nobel prizes in Physics awarded to eleven laureates whose names are mentioned below with an asterisk* (two stars** in reactive scattering are used for Nobel laureates in Chemistry!). Among these achievements are the verification of the Maxwell-Boltzmann velocity distribution of gaseous atoms (O. Stern*, 1911), the discovery of the space quantization (O. Stern* and W. Gerlach, 1922) and its important applications in nuclear magnetic resonance (I. Rabi*, 1938). The NMR technique was extended to liquids and solids (F. Bloch* and E. M. Purcell*, 1945) and later remarkably developed to determine structures of proteins and observe even fleeting thoughts in human brains by magnetic resonance imaging. Other atomic beam experiments of the highest interest also exploited space quantization, for example in the resolution of the splitting in the fine structure of the first electronically excited H atom (W. Lamb* and R. Retherford, 1947). This led to a major theoretical advance, the development of modern quantum electrodynamics. Likewise the magnetic moment of the electron was measured revealing a 0.1 % discrepancy, small but highly significant, from Dirac’s quantum theory (P. Kusch*). Also, optical pumping was discovered using a sodium beam (A. Kastler*, 1950), although this application is not restricted to molecular beams. Finally the combination of an ammonia beam (NH₃) and an electric field, instead of a magnetic field, provided space quantization and state selection which have led to the invention of the maser and hence the laser (Ch. Townes* and also N. Basov* and A. Prokhorov*, in the 1950s). The historical beam experiments listed above are discussed extensively (except for optical pumping and lasers) in a classic book “Molecular Beams,” published in 1955 by N.F. Ramsey* (1989) and briefly described in this volume in the introductory article by Dudley Herschbach** (1986).

Chemistry in crossed molecular beams, under single collision conditions, was not shown to be feasible until after the second half of the century began (Bull & Moon, 1954; Taylor and Datz, 1955). The early era dealt with alkali atom
reactions, by virtue of the ease of detection by means of surface ionization and the high yield of many of these reactions, shown already in the 1920s by Michael Polanyi. Happily, during the past 30 years, beam experiments have gone far beyond the pioneering alkali age, probing a host of collision processes involving exchanges of momentum, energy, charge, or atoms. Most of these advances resulted from marked improvements in detection capability (dating from 1968 and largely due to Y.T. Lee**) as well as the development of versatile supersonic beams based on theoretical predictions by A. Kantrowitz and J. Grey (1951). When compared with effusive beams, this powerful technique allows great enhancements in density, intensity, velocity (or de Broglie wavelength) resolution, and the kinetic energy. By heating or cooling the nozzle, as well as having the additional option of seeding the gas of interest and even clustering it during the expansion, the sources can be operated as monochromators and over a wide energy range, of about 0.01 to 50 eV, or higher for large clusters. The use of light atoms, such as helium, at low kinetic energy, results in de Broglie wavelengths comparable to interatomic distances (of order one Angstrom unit) and hence an exceptional tool to probe solid surfaces.

The very low temperature achieved in the free jet is extremely useful in high resolution molecular spectroscopy which can be performed down to the kelvin range at the maximum source pressure allowed by the largest diffusion pumps (J.B. Fenn, 1963, 1996). The millikelvin range is accessible, at least for the translational temperature, when higher pressure is acceptable by exploiting the free jet shock wave structure to shield the expansion in a “zone of silence” unaffected by the background gas (R. Campargue, 1964, 1984). Such a method has been used beautifully in the pioneering works in molecular jet spectroscopy (R.E. Smalley**, D.H. Levy, and L. Wharton, 1975-1980) and later in work using the pulsed jet technique (W.R. Gentry, 1978). Finally, it should be pointed out that the great advances during the last decades, and mainly during the recent years, have been due to the progressive coupling of atomic and molecular beams with lasers (J.C. Polanyi**, 1986) and other light sources such as the synchrotron radiation and the free electron laser. Thus, spectacular developments have been obtained after initial studies on the physics of the free-jet expansion involving the translational and internal energy relaxation processes. The most important research works have been devoted to molecular jet and beam spectroscopy, photodissociation, single-collision reactions, van der Waals molecules, clusters and nanoparticles, as well as gas-surface interactions. The impressive accomplishments on chemistry-reaction dynamics have been rewarded by the 1986 Nobel Prize in Chemistry awarded to D.R. Herschbach**, Y.T. Lee**, and J.C. Polanyi**.
The predecessor book “Atomic and Molecular Beam Methods” (1988 and 1992), edited by Giacinto Scoles, was presented by the Editor as “more concerned with describing how to carry out beam experiments than describing the Physics and Chemistry, underlying them”. The present volume will be complementary to this excellent predecessor from two points of view: (i) the improvements and novel techniques obtained since 1988 for using atomic and molecular beams and, increasingly, their combination with lasers, (ii) the state of the art in 2000 largely described in up-to-date review articles, as well as in specialized articles on original works, all dealing with beam research and applications in Physics and Chemistry, with an extensive coupling with lasers.

The present book was born as a project early last year after the scientific organization, by the Editor, of the 21st International Symposium on Rarefied Gas Dynamics, held in Marseille, France, July 26–31, 1998 (RGD-21). It should be pointed out that the supersonic beam techniques have been developed largely in the RGD community alongside the work of the aerodynamicists. Also their cooperation with physicists and chemists, during about 30 years, has been useful to get the balance between experiment and theory in the RGD symposia. Nevertheless, during the last decade, the work in RGD have more and more been concerned with only theoretical aspects of flows of rarefied gases: kinetic theory, Boltzmann equation, numerical solutions, and Monte Carlo methods. In order to include many more experimental works in the RGD-21 symposium program, the Editor of this book organized a third session with the scope and style of the Molecular Beam Symposia issued from the RGD series a few decades earlier. This has been possible thanks to 34 individual invitations accepted spontaneously by experts in the field, who together with resulting additional participants, allowed us to include 62 papers in the Molecular Beam session of the RGD-21 symposium.

This volume arose initially as only an alternative to publish separately in about 300 pages (instead of 1000 in the present book) this body of predominantly experimental work alongside the theoretical treatments on rarefied gas flows and aerodynamics. A much better venue has been found later by undertaking an ambitious project consisting of collecting in a topical volume the outstanding works in Atomic and Molecular Beams, reflecting the state of the art 2000. This tremendous project was encouraged by the manifest accomplishments in the field, rewarded by 11 Nobel prizes during the last 13 years, and also by the kind support of six Nobel laureates, as well as many other important scientists who joined successively the project in the course of 1999 and 2000.
Finally, the current state of the art in Atomic and Molecular Beams, is described in the volume by scientists at the highest level and worldwide groups in the field:

- four Nobel laureates and other important contributors invited individually,
- invited speakers of the Molecular Beam session at the RGD-21 Symposium, having acted as the initial and essential “cristallites” to attract and gather together all the contributors,
- invited speakers of five Gordon type Conferences held in 1999:
  - Physics School on Atom Optics Applications, Les Houches, France, May 23–28, 1999
  - COMET 16, Perugia, Italy, June 25–27, 1999
  - 31st EGAS (European Group for Atomic Spectroscopy), Marseille, France, July 6–9, 1999.
  - Dynamics of Molecular Collision Conference, Lake Harmony, USA, July 18–23, 1999

The volume contains 68 invited contributions including a few surveys. The papers extend to work throughout the 20th Century and include up-to-date reviews corresponding to the seven sections of the book, and a large variety of specialized chapters on the advances on Atomic and Molecular Beams largely coupled with lasers. Despite being invited, the articles have been carefully reviewed at least by two or three experts and then largely revised by the contributors. The great interest of the book is due essentially to the diversity of modern and fundamental subjects in Physics and Chemistry, as well as their actual and potential applications, the high scientific level of the contributions, and the great effort of the authors to improve the manuscripts, especially for being accessible to non specialists and address a wide audience. The 68 invited contributors and their coauthors total 231 authors originating from 17 countries. The articles and the seven Parts of the book are summarized, reviewed, highlighted and even enlarged in the Foreword including, as in the book, the following successive sections:

**Introductory Perspectives** by D.R. Herschbach (Nobel Prize in Chemistry, 1986) Atomic and Molecular Beams in Chemical Physics: A Continuing Odyssey

**Part I:** Laser Cooling and Manipulation of Atoms and Molecules – Atomic and Molecular Optics and Applications Foreword by J. Dalibard and C. Cohen-Tannoudji (Nobel Prize in Physics, 1997)
Preface IX

Part II: Translational and Internal Energy Relaxation in Supersonic Free Jets, Including Possible Alignment and Condensation Phenomena

Part III: Photodissociation Dynamics and Electronic Spectroscopy in Molecular Beams: From Simple Molecules to Clusters and Ions


Part V: Clusters and Nanoparticles: Diffraction, Size Selection, Polarizability, and Fragmentation by Photodissociation, Electron Impact, and Atom Collision

Part VI: Spectroscopy and Reaction Dynamics of Molecules Isolated, Cooled (or Conditioned) by Techniques of Molecule, Cluster, Droplets, or Liquid Beams

Part VII: Interactions of Molecular Beams and Cluster Beams with Surfaces, and Applications


We would like to express our deep appreciation and gratitude to Claude Cohen-Tannoudji*, Dudley Herschbach**, John Polanyi** and Ahmed Zewail,** for their huge encouragement and stimulation of the project and finally for enhancing, in 136 pages, the scientific level and the interest of the volume. Our appreciation and gratitude are extended to Will Castleman, Helmut Haberland, Joshua Jortner, Yuan Lee**, Rick Smalley**, Dick Zare and other leading scientists, not able to join us despite of attempts of most of them, but generous in their support for our project. Obviously, our thanks are also largely due to all the other invited contributors and their co-authors for reflecting thoroughly and so beautifully the various perspectives of Atomic and Molecular Beams. Additional acknowledgements are addressed to 41 authors, and, especially, 36 non contributors (together listed below) all having reviewed carefully and improved widely the manuscripts.

We are indebted also to the Organizations and Laboratories having supported the preparation and finally the realization of our ambitious project, as well as the sponsors for allowing one free copy of the volume to be offered to the authors for each contribution. Finally, our sincere acknowledgements are given to Springer-Verlag and especially to the persons mentioned by names below for their flexible and supportive arrangements during the preparation and publication of this book.

In conclusion, it is a happy outcome, for the contributors as well as the editor, to finally heft a lovely volume that provides a rather comprehensive (and comprehensible!) topical survey of the state of the current art in Atomic and Molecular Beams. This research field has been commemorated
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by Nobel Prizes awarded to 21 Laureates during the past century, including eleven during the last thirteen years. We are proud and honored that most of these Laureates are still active in our community and several have contributed to our volume. Finally, in view of the recent outburst that yielded seven new Laureates in just the past four years, it seems likely that other Nobel Prizes will be awarded to some of the outstanding contributors to this volume.

Roger Campargue, Editor

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Beginning with an introductory survey "Atomic and Molecular Beams: A Continuing Odyssey" by Dudley Herschbach and concluding with a study of future prospects "Looking Ahead: Macro, Micro and Nanobeams" by John Polanyi, this topical book presents the current state of the art of atomic and molecular beams. This Foreword is intended to complement the Preface by summarizing, reviewing, highlighting and even extending the seven parts of this volume. A grateful acknowledgement is due to those who contributed to the summaries and helped the editor to write this Foreword.

Drawn from among the authors and referees of the articles in this volume, these experts wrote two of the summaries in their entirety and provided corrections, completions, and improvements to the remainder. We are particularly indebted to the following persons: J. Baudon, U. Buck, Ph. Cahuzac, B. Girard, G. Hancock, D. Herschbach, A. Hodgson, A.W. Kley, K. Liu, R. Miller, P. Pillet, J.C. Polanyi, T. Seideman, S. Stolte, J.P. Schermann, B. Shizgal, and J.P. Toennies.

Introductory Perspectives: Atomic and Molecular Beams in Chemical Physics: a Continuing Odyssey by Dudley Herschbach

In his fascinating Introductory Perspectives, addressed to nonspecialists, Dudley Herschbach (who shared the 1986 Nobel Prize in Chemistry with John Polanyi and Yuan Lee, "for the development of a new field of research in chemistry-reaction dynamics") provides what he terms "appetizers for a smorgasbord." After sketching the historical evolution of research employing atomic and molecular beams in Physics and Chemistry, he serves up morsels representative of the seven parts of this book. His "menu" includes the elucidation of molecular dynamics in interstellar clouds, in meteor trails, in clusters generated in supersonic expansions, and in surface-catalyzed reactions. Other appetizers exemplify techniques for enhancing resolution and control of the intimate mechanics of collisions. Among these are means to arrest molecular rotation; to slow translation markedly, thereby endowing molecules with pronounced wave properties; and to select by laser light a specific reaction pathway, thus fulfilling a modern alchemical quest. As well
as emphasizing thematic motivations and methods, these enticing vignettes also convey much about the adventurous spirit of a continuing odyssey.

Part I: Laser Cooling and Manipulation of Atoms and Molecules – Atomic and Molecular Optics, and Applications

Part I is devoted to the present state of the art of laser manipulation and cooling of gas phase matter. The interaction of atoms with coherent light has been studied since the invention of the laser. Nevertheless, apart from extensive study of the (undesired) Doppler effect, little attention was devoted to the effect of light on centre-of-mass motion of the atom other than the pioneering work on "lumino-réfrigération" (A. Kastler, 1950). The use of the radiation pressure of light to slow down and cool atoms was introduced only in the seventies and paved the way to the development of atomic traps. During the last fifteen years, a wide variety of devices combining cooling and trapping, such as the magneto-optical trap (MOT), have been developed, with applications ranging from new time standards (atomic clock) to the realization of Bose-Einstein condensation. At very low temperature, provided that the density is sufficient, the quantum character of the statistics becomes dominant. For identical bosonic atoms this may result in an accumulation of almost all atoms in the ground state of the trap, leading to a macroscopic wave function – a Bose-Einstein condensate.

The remarkable progress in atom cooling technology going beyond all the standard limits, down almost to the nanokelvin range, was acknowledged by the 1997 Nobel Prize in Physics awarded to S. Chu, C. Cohen-Tannoudji and W.D. Phillips.

The laser cooling technique for atoms cannot be extended directly to molecules, but laser-assisted cold atom collisions can form ground state molecules through photoassociation. In this process, one photon is absorbed to form resonantly excited dimers. For well-chosen excitation configurations, photoassociated excited molecules spontaneously decay to the ground state. This method opens access to high-resolution photoassociative spectroscopy and provides information about the long-range parts of internuclear potentials that is not available from conventional spectroscopy. The photoassociation technique extends the field of ultracold diluted matter to molecules in the microkelvin range, with promising applications in optics and interferometry, as well as in the development of an ultracold photochemistry. Bose-Einstein condensation of a molecular gas is at present being actively pursued.

The field of atom optics has similarly reached maturity, providing new tools for fundamental research, as well as for applied purposes. Polarization or
Stern-Gerlach interferometers are based upon the atomic spin evolution in a magnetic field. The very high sensitivity of such devices in a spin-echo configuration is evidenced by the study of inelastic and quasi-elastic $^3$He scattering by clean and adsorbate-covered gold surfaces. The versatility of Stern-Gerlach interferometers is demonstrated by the variety of interference effects that have been produced by special magnetic configurations. Atomic mirrors are routinely produced and serve as a key optical element in a number of experiments. For example, at very low energy, atoms are prevented from sticking to the surface by the phenomenon of quantum reflection. An intense atomic micro-probe has been produced by focusing helium atom beams by a concave mirror (a crystal surface deformed by a static electric field). Finally, atom lithography is now going beyond the resolution of conventional lithographic techniques. Sub-micrometric structures can be deposited on a substrate, or engraved on a resist, using a phase mask, i.e., a standing optical wave with a resolution of a few tens of nm. Interference of atomic and molecular wave packets has been observed using time delayed ultra-short laser pulses.

The well-established techniques of atom optics cannot be extended to molecular systems. Nonetheless, recent work illustrated the possibility to spatially manipulate molecules by use of the intensity property of laser light. The newly introduced field of molecular optics is based on the interaction of an intense, nonresonant laser field with the molecular polarizability tensor. Since the polarizability of molecules (by contrast to that of atoms) is anisotropic, a polarized laser field (where both spatial and orientational gradients are available) can serve to align molecules along given space-fixed axes, as well as focus their center-of-mass motion in space.

**Part II: Transnational and Internal Energy Relaxation in Supersonic Free Jets, Including Possible Alignment and Condensation Phenomena**

The supersonic expansion of neutral atoms, or molecules, is a very useful technique to investigate relaxation phenomena with possible ultracooling, special alignments of molecules, and interesting nonequilibrium effects on the internal degrees of freedom, including population inversions as exploited in a gas dynamics laser. Furthermore, this technique is uniquely suited to create and study “exotic” species such as van der Waals molecules, clusters, and nanoparticles. The physics of supersonic free jet expansion is extended to plasmas (first state of the matter and major part of the Universe) ranging from the astrophysical sizes (supernovae, solar flares) to intermediate lengths as used in nuclear fusion (Tokamak) and plasma chemistry (DC, RF, and microwaves torches), and to very small scales such as in cathode spots and micro-sized laser spots for laser ablation. Plasma expansions, for tem-
temperatures not exceeding about 20,000 K (low degree of ionization) appears to be describable (at least for neutral species) in terms of local density, velocity, and translational temperature, analogous to a neutral gas expansion. Electronic relaxation, as deduced from fluorescence measurements, leads to excitation temperatures close to the calculated electron temperatures but much higher than the measured and calculated translational temperatures. The applications of these plasma flows include such topics as plasma chemistry, deposition and surface modification, also the simulation of space experiments in low earth orbit or re-entry, and the generation of beams of H (proton sources), O (atmosphere and space interests), and metastable nitrogen molecules for the growth of nitride semiconductors.

The relaxation of O^1D, as produced in O atom sources of atmosphere interest, is studied experimentally in argon and theoretically in neon using a solution of the Boltzmann equation, as well as a Monte Carlo simulation. In the last few decades, the cooling and the natural alignment of rotational angular momentum, in seeded supersonic jets, has been investigated both experimentally and from a quantum mechanical view. The internal energy distributions in molecules, such as K_2, HBr, and OH, seeded in argon or nitrogen free jets, deviate from rotational and vibrational equilibrium Boltzmann distributions at the translational temperature. As shown using the techniques of laser induced fluorescence (LIF) and resonance-enhanced multiphoton ionization (REMPI), the overpopulations increase with both the rarefaction in the expanding flow and the rotational quantum numbers. Nitrogen is more efficient than argon as a relaxant of rotational states, but this may be influenced by possible Ar condensation enthalpy. Complete diagnostics and mapping of CO_2 and N_2 free jets are obtained by the Raman technique which provides the absolute local densities and local vibrational and rotational temperatures. These data, together with the momentum and energy conservation, make it possible to deduce the corresponding translational temperatures, flow velocities, and condensation energies. More information on the aggregation is monitored through Rayleigh scattering. Finally, the average size, composition, and structure of mixed Ar-N_2 clusters, as well as the amount of uncondensed monomers, can be deduced by coupling beam scattering in gases and at surfaces, with high energy electron diffraction.

Part III: Photodissociation Dynamics and Electronic Spectroscopy in Molecular Beams: From Simple Atoms to Clusters and Ions

Studies of photoexcitation of species in molecular beams continuously reveal new and exciting phenomena, and the results reported in Part III are no exception. Much progress results from new or refined techniques, and in this section two themes are dominant.
The first area is the probing of the photodissociation dynamics of small molecules, particularly with photoionization detection (REMPI). The technique provides a highly selective and sensitive method for extracting both the scalar and vector properties of a photodissociation event. Scalar properties are those of fragment energies, available through the spectroscopic signatures of quantum states and of the kinetic energies from time-of-flight measurements. Laser light also has inherent vector properties – for example it has a propagation vector, simply the direction of the laser beam, and is normally polarized so that there exists an electric vector which is perpendicular to the propagation direction. These properties can be used to unravel the correlations between parent transition moments, fragment velocities and angular momenta - for example, does the departing fragment spin away from the parent like a frisbee or does it take off like a helicopter? Velocity map imaging, state selection of reagent molecules, and femtosecond excitation feature as recently refined techniques to explore in ever increasing detail the properties of the dissociating molecule.

The second area concerns the study of the dissociation dynamics of van der Waals complexes as revealed by the spectral signature of fragmentation paths. Such molecules can most easily be prepared when their component species are co-expanded, from a high to a low pressure environment, to form a jet and then a beam, with the expansion providing exactly the cooled conditions required for the complexes to survive. Careful reagent preparation and precise spectroscopic probing, inevitably with lasers, are the keys to successful interpretation of the behaviour of electronically excited complexes. The electronic spectra of van der Waals complexes, involving metal atoms, can be used to infer the non-bonding interactions of both the ground and excited states, of relevance for an understanding of the spectra of atom-doped solid matrices. Molecular beams can yield internally cold species, and a striking example is in the formation of cold cations of polycyclic aromatic hydrocarbons (PAHs) for spectroscopic investigation. This example illustrates an increasingly important feature of molecular beam technology, that the results can have pronounced importance outside the field of laboratory spectroscopy. PAHs have been suggested as the carriers of the long known Diffuse Interstellar Bands, and only recently has it been possible to prepare such species for laboratory characterisation.

Dissociation of simple molecules such as O₃, N₂O and NO₂, has important atmospheric consequences. For ozone, the observation of both vibrationally mediated and spin forbidden photodissociation processes through molecular beam time-of-flight methods, has helped to lead to a quantitative reassessment of the oxidizing capacity of the troposphere, and for N₂O a detailed knowledge of its photolysis is required to understand its global budget and hence its participation in ozone loss processes. These examples of the ap-
plication of molecular beam and laser techniques show the relevance of such studies to problems in applied photochemistry.

**Part IV: Dynamics of Elementary Collisions and Femtochemistry: Theory, Real-Time Probing, and Imaging of Crossed-Beam Reactions**

Chemistry is a subject of bond breaking and bond making. In addition to its fundamental importance, gas phase chemical dynamics also has a wide range of applications in many practical disciplines such as combustion, atmospheric chemistry, astrophysics, plasmas, and chemical vapor deposition. Recent years have witnessed a remarkable progress in our deeper understanding of the microscopic details of chemical reactivity. Novel experimental techniques make it nowadays feasible to actually watch how the chemical transformation occurs (seeing is believing) and to carry out fully quantum state resolved studies for a wide range of chemical systems far superseding the former limitations of the alkali age. The combination of molecular beams and lasers has played a pivotal role in this advancement. The crossed-beam technique allows experimentalists to measure the product, speed, and angular distributions under well defined single-collision conditions. The implementation of lasers in the beam experiment provides the additional full capability of quantum state, polarization, and real-time resolution in interrogating and/or manipulating a bimolecular scattering event. The experimental progress has been accompanied by an equally impressive development in theory. In fact, the hallmark of recent advances in the field of chemical dynamics is the synergy of experiment and theory.

Part IV starts with a broad review by A. H. Zewail, the 1999 Nobel laureate in Chemistry. His revolutionary femtochemistry techniques make it possible to follow continuously the motions of the atoms in molecules, from reagents to products, by taking femtosecond real-time snapshots of the chemical transformation which typically occurs within a few pico-seconds. This feature article is then followed by a theoretical perspective on femtochemistry and by an alternative optical-collision approach in which the colliding pair is optically interrogated directly while they are still in close encounter.

The remaining eight articles focus on the recent advances and applications of crossed-beam techniques in exploring various collisional processes with unprecedented fine details. The method of counterpropagating pulsed beam scattering, combined with high resolution ion time-of-flight (TOF) analysis and state-specific resonance-enhanced multiphoton ionization (REMPI) detection, is reviewed and illustrated by the accessible state resolved integral and differential cross sections and even single collision induced alignment. Then a powerful multiplexed ion imaging detection scheme is presented in
which the state-specific product, after being ionized, is projected onto a position sensitive detector so that its entire angular distribution can be revealed simultaneously. The stereodynamic effects are explored in the rotational energy transfer of NO+ Ar using an oriented molecular beam. Thus, it is found that, for the formation of highly rotationally excited products, a collision at the O-end is more effective than a collision at the N-end, in agreement with theoretical prediction. Also the Doppler-selected TOF method is introduced, in which the conventional Doppler and high resolution ion TOF techniques are blended in an innovative manner, so that the product three dimensional velocity distribution, in the center-of-mass coordinates, can be mapped out directly. Its application to the study of a prototypical insertion reaction is beautifully illustrated. Another chapter highlights recent applications of an ultra-high resolution translational energy spectroscopy, the H-atom Rydberg tagging TOF technique achieving fully state-resolved angular distributions. Also the reaction kinetics are studied in uniform supersonic flows at very low temperatures and the results obtained for a variety of molecular processes are highly relevant to astrophysical chemistry. The last two articles present ion/neutral crossed-beam collisions. In particular, the dependence of the reaction cross section on the initial collision energy is studied for ion-molecule reaction at low energies. In a combined experimental and theoretical study of an ion-atom collisional system, the measured and calculated cross sections and its energy dependence are in good agreement.

Finally, these eleven chapters together provide a quick, yet balanced glimpse of state-of-the-art crossed beam techniques, and offer exciting new perspectives on the fundamental nature of chemical transformation, as we march into the New Millennium.

**Part V: Clusters and Nanoparticles: Diffraction, Size Selection, Polarizability, and Fragmentation by Photodissociation, Electron Impact, and Atom Collision**

This section deals with the physics of clusters, a new state of matter between isolated atoms and molecules and the condensed phase of bulk matter, as generated in jet and beam experiments. These aggregates differ considerably both from their original constituents and from bulk matter in several ways. Their physical and chemical properties are strongly dependent on the number of atoms in the cluster, and even for one specific size there may exist a considerable number of different isomeric structures. In spite of their finite number of particles, clusters can undergo phase transitions and exhibit collective excitations. In contrast to bulk matter, a large fraction of their atoms or molecules are on the surface. All these properties make them very attractive for investigations which provide a new microscopic under-
standing of macroscopic phenomena such as solvation, chemical reactions, and catalysis.

In some cases, cluster research even resulted in the discovery of new materials. The most prominent example is the discovery of a new modification of carbon, the fullerenes $C_{60}$ and $C_{70}$, in a molecular beam experiment in which laser vaporized graphite was seeded and expanded in helium. The apparatus was not expressly designed for the study of carbon but for the production of silicon and germanium clusters. This accomplishment has been acknowledged by the 1996 Nobel prize in Chemistry awarded to H.W. Kroto, R.F. Curl and R.E. Smalley. Aside from these strongly bound fullerenes, clusters are also observed for weakly bound van der Waals and hydrogen bonded, as well as for ionic and metallic systems. The latter ones are of special interest, since such bond does not exist for small molecules so that the transition to metallic behavior is an important research goal.

The articles in Part V deal with a variety of systems ranging from small clusters, where fundamental quantum aspects are predominant, to nanoscale particles with properties relevant for applications. An important topic is the production of neutral, size-selected clusters. Here the most advanced methods are discussed which include examples of small rare gas clusters (especially He) produced by diffraction from a free-standing transmission grating, or which are generated by deflection from an atomic beam with additional velocity analysis. The results of measured and calculated dipole polarizabilities of alkali metal clusters reveal, already for small cluster sizes, the transition to metallic behavior based on non-local effects during the interaction. This also clarifies the optical response of these systems.

Dynamical processes are studied in the fragmentation of argon clusters by electron impact, the photodissociation of water clusters, and in a detailed series of collisions of metal cluster ions with atomic partners, using state-of-the-art techniques. The large fragmentation during the ionization process is essentially caused by the energy release when the system undergoes the transition from the weakly interacting neutral to the strongly bound ionic configuration. The photoabsorption and the subsequent dissociation of water clusters is strongly dependent on the formation process. In collision-induced dissociation processes with rare gas atoms, the different mechanisms for impulsive and electronic energy transfer are elucidated as a function of the cluster size. In charge transfer experiments of metal, metal oxide, and metal hydroxide ions with metal atoms, the onset of the non-metal to metal, or other bonding behavior, is observed. Another important problem, which is addressed in several contributions, is how the energy is distributed after the clusters collided with electrons. Applications range from electron attachment to molecular clusters, via the radiative cooling of fullerenes, to
the assessment of internal energy distributions for solvated metal ions and the fragmentation of these systems by evaporation.

The small molecular species allow us, aside from solving problems of fundamental interest, to study also questions relevant to solvation and atmospheric chemistry, whereas larger covalent species are investigated with the aim of designing nanostructured materials with novel electronic properties which can be exploited for various applications, particularly in optoelectronics. As an example, nanosized silicon crystallites are generated by combining a laser-driven flow reactor containing gas phase precursor molecules (SiH₄ in He) with a supersonic expansion to form a beam of pure silicon clusters with velocities strongly dependent on their size.

Part VI: Spectroscopy and Reaction Dynamics of Molecules Isolated, Cooled (or Conditioned), by Techniques of Molecule, Cluster, Droplet, or Liquid Beams

Considerable progress has been made in recent years in the development of experimental methods for studying large clusters, nanodroplets, and liquid beams. These media are not only interesting in their own right, but are also providing novel spectroscopic matrices capable of isolating, ultracooling (or conditioning at the gas-liquid beam interface) molecules, mediating chemical reactions, and forming new molecular aggregates. Free jet expansions can be used to make clusters of quite large size (10³ to 10⁵ atoms or molecules) for the rare gases and hydrogen. These large clusters generally cool by evaporation and, with the exception of helium, are thought to be effectively solid.

At low pressures, helium remains liquid to absolute zero and the corresponding nanodroplets are the only ones that are known to be liquid under molecular beam conditions. These large clusters and droplets can be doped with other atoms and molecules by passing them through a "pick-up cell", namely a chamber containing a low pressure of molecules of interest. For a typical pick-up cell 10 cm in length, one microtorr pressure is needed to capture a single molecule. While the alkali atoms have been shown to reside on the surface of liquid helium droplets, molecules are immersed in the helium and thus reside on the inside. Owing to the weak interactions between an immersed molecule and the helium, the environment is both homogeneous and non-dissipative (superfluid) so that high resolution spectroscopy is often possible. The temperature of the clusters and droplets depend directly upon the binding energy of the matrix atoms or molecules, resulting in 4 K for hydrogen clusters and 0.38 K for ⁴He. Even lower temperatures (0.15 K) are possible using ³He, owing to the higher zero point energy of this system, which reduces the energy required to evaporate an atom. In
contrast with conventional matrix spectroscopy, liquid helium gives much smaller solvent frequency shifts, again owing to the weak interactions, and the molecules undergo free rotation. Also the technique is useful in high resolution spectroscopy on collimated beams of cold molecules spontaneously desorbed from droplet surfaces, or on molecules laser desorbed from liquid beams.

In the case of supercooled hydrogen droplets, the coagulation of CO would argue also in favor of a matrix of metastable superfluid liquid. Thus, the technique of using finite-size, isolated and ultracold droplets appears as an exciting new general approach to study both properties of the liquid solvent and interactions between the molecule and solvent, as well as providing a suitable growth medium to form and investigate novel cluster structures. Liquid beams offer another interesting approach for studying the liquid-gas interface and areas such as the dynamics of solute molecules on solution surfaces. Fragile biomolecules, such as DNA bases and their pairs, or peptides, can be seeded in pulsed supersonic free jets, without using excessive temperatures. They are just now being investigated for the first time by high resolution spectroscopy, using REMPI detection combined with laser desorption obtained by heating the substrate rather than the molecules of interest.

Finally, the clusters constitute novel nanoreactors for studying solvation effects on chemical reactions at the microscopic level, as shown on neon clusters with dramatic increases of reaction rates, as compared to those in the gas phase.

As with all good ideas, this is a divergent field that is finding applications in many different areas.

**Part VII: Interactions of Molecular Beams and Cluster Beams with Surfaces, and Applications**

Molecular beams offer a powerful technique for studying surfaces and surface phenomena, providing a flexible tool which is entirely specific to the surface. Since their adoption to investigate surfaces, beam techniques have helped to transform our understanding of surface and phonon structure, energy transfer, molecular dissociation and chemical reactions, giving detailed information against which new models can be tested. The combination of molecular beam scattering with state resolved techniques (such as LIF and REMPI) has opened up gas-surface dynamics to detailed scrutiny and is providing a unique understanding of how small molecules and clusters scatter and dissociate at surfaces.
The applications described here range from simple reflection of noble gas atoms to the impact of large and complex species on surfaces. The opening chapter describes theoretically the unique environment and chemistry which occur during high energy cluster-surface collisions. In this case the surface collision reflects an incoming cluster back on itself, creating a super hot, dense gas in which each collision nevertheless remains essentially isolated. The high energy and gas density created in the reflecting cluster promote multi-centre reactions, which do not occur directly under thermal conditions, while preserving new products as the cluster disintegrates.

All the other contributions focus on modern research into gas-surface interactions. These begin with a chapter describing the reflection and adsorption of a simple molecule at an inert surface, using beam and state selective detection to probe reaction dynamics and reveal how small molecules dissociate and react at metal surfaces. Molecular beam scattering is used to investigate the energy exchange as a molecule approaches a dissociation barrier, providing information on the shape of the potential energy surface and the role of short lived molecular states during scattering. Also the reverse process is described: the recombinative desorption of two adsorbed atoms to form a diatomic molecule. Nitrogen bond formation and product desorption are investigated using state selective techniques to explore the dynamics of surface recombination, using detailed balance arguments to link desorption to dissociation and predict how molecular motion influences the dissociation probability.

Subsequent chapters describe experiments in which more complex species interact with a surface under a variety of conditions. For the scattering of low energy van der Waals clusters of mixed rare gases, from a graphite surface, attention is focussed on the enrichment of the surviving species. Electrical charging of clusters is described for the more cohesive water clusters, scattering from a number of solid targets. A fullerene may be considered as a very strongly bound cluster but to regain a similar energy transfer to that of a lightly bound cluster the interaction energy of a fullerene must be much higher, and charge exchange and ionization can easily occur. Electron emission from clusters colliding with graphite reflects electronic transitions during scattering and the neutralization dynamics. This is analysed by combining experimental and theoretical approaches.

Next, the growth of surface films is performed by supersonic free-jet epitaxy of wide bandgap semiconductors of particular relevance to III-N deposition (nitrogen), and also by carbonization of Si surfaces during reaction with alkenes, as shown by beautiful chemical map analysis using X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscope (SEM).
Looking Ahead: Macro, Micro and Nanobeams by John Polanyi

In the final chapter entitled "Looking Ahead", John Polanyi (who shared the 1986 Nobel Prize in Chemistry with Dudley Herschbach and Yuan Lee, "for the development of a new field of research in chemistry-reaction dynamics") considers some tempting approaches to molecular-beam chemistry that he refers to as "Macro, Micro and Nanobeams." He begins with the "micro" in which the pulsed beam sources would be located fractions of a millimetre apart, so as to maximise the density in the crossing region. This could be achieved by pulsed laser-induced desorption of the beams from tilted crystal faces. Unprecedentedly low reactive cross-sections should be measurable.

Microbeams lead naturally to nanobeams in which the interacting photofragments encounter one another after travelling a distance measured in angstroms. This approach, termed Surface-Aligned Photochemistry, SAP, has been realized in a number of laboratories.

Particular interest attaches to the cases in which the photorecoiling molecular fragment is aimed in a downward-directed beam. In Localised Atomic Scattering, LAS, such a beam (in contrast to the generalised beam + surface scattering described in Part VII) is aimed with a restricted impact parameter at preferred atomic sites on the surface, scattering therefore at angles far from specular.

Still more interesting is the analogous case in which the atomically-localised collision with the surface results in chemical reaction at the surface, this being Localised Atomic Reaction, LAR. The site of the parent molecule relative to the site of the new bond at the surface will have much to tell us about the molecular dynamics of the surface reaction, since it will allow us to map the molecular motions onto the substrate.

Finally, moving back from nano to macro, mention is made of beam chemistry on the largest scale that occurs when "pulsed" dense clouds of interstellar gas encounter one another, leading, one may presume, to characteristic forward, backward or sideways scattering (see Dudley Herschbach's opening article) depending on the molecular dynamics of the all-important interstellar reactive events.

Not surprisingly phenomena on the grandest-scale depend upon the finest molecular details. If this were not the case, why would we study molecular beam physics and chemistry?
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