Over the years, the editors and authors of the *Annual Review of Physical Chemistry* series have attempted to provide us with a broad definition of physical chemistry in an era of growing international collaborations and subsequent blurring of the sharp boundaries between disciplines. The present volume starts with reminiscences of a spectroscopist, William Klemperer who describes how physical chemistry (read spectroscopy) has grown in front of his and his colleagues' eyes at Harvard. He narrates how rotational spectroscopy in cold molecular beams has helped us understand interstellar chemistry. This introductory chapter, although well written, is more of a technical account than personal. We wonder if a scientist only remembers the scientific achievements of the past and not the personal incidents that were associated with it along with the personalities!

Most of the articles in the present volume deal with gas phase spectroscopy and dynamics of one kind or other. Herbst as well as Sims and Smith have dealt mainly with rates of gas phase reactions at low temperatures. Herbst's motivation being guided by chemistry in interstellar medium, he concentrates on ion–molecule reactions for generating exotic species and rules out the possibility of neutral–neutral reactions at the low temperature and density of the interstellar medium. Sims and Smith, on the contrary, discuss elementary chemical reactions of neutral reactants at temperatures as low as 13 K. Several examples of molecular energy transfer at low temperatures are discussed.

Gas phase photochemistry and dissociation/reaction dynamics are described, at least, in four experimental and five theoretical chapters. In his article, Bernstein describes intracluster electron and proton transfer, vibrational relaxation, predissociation and radical additions with suitable examples. Farrar has discussed ionic reactions with a special emphasis on proton and hydrogen atom transfer reactions of the atomic oxygen anion. Gas phase $S_2$ 2 reactions have also been included. Mode-selective enhancement of chemical reactions of acetylene and ammonia cations with other species have been reviewed. Recent developments on two-dimensional imaging of a chemical reaction as if proceeds has been reviewed by Heck and Chandler. Quantum state distribution of a product and the velocity correlated to that distribution can simultaneously be measured by this new method. The authors present in detail how to convert the image into useful information. The instrumentation aspect has been emphasized so that the readers can follow the procedure with ease. This is an excellent article and discusses both orientation and alignment in uni- and bimolecular reaction processes. In another article, Loesch has reviewed recent progress in reactive beam collisions with special importance to orientation and alignment. Two techniques have been described, a brute force technique and an infrared laser-based optical technique, to orient and align molecules in a supersonic beam. The reactions of alkali metals with HF, ICl and CH$_2$X (X=I or, Br) are discussed along with the relevant theoretical results.

Theoretical studies of polyatomic reaction dynamics have been illustrated by Bowman and Schatz. In this account, the authors have concentrated on four or more atom reactions. Currently, all efforts on experimental and theoretical fronts are focused on four-atom reactions in order to unravel the mechanism of these reactions. This is a timely review dealing with quantum and quasiclassical methods of calculating reaction rates and cross-sections. Adequate comparisons between theoretical and experimental results have been made in order to put the concerted world-wide efforts in this field in perspective. An equivalent but different approach of modelling three and four atom chemical reactions has been described by Jackson. The wave packet reactive scattering approach pioneered by Heller and improved by many has been discussed. Extension of the wave packet dynamics calculations to gas-surface reactions has been dealt with. In another article, Jolicard has discussed yet another method, the effective Hamiltonian for molecular dynamics calculations. This method, developed in the 1960s gained a lot of attention in the '70s. The author has discussed the theoretical foundation in detail. Application of vibrational energy redistribution and photodissociation of van der Waals molecules, as well as femtosecond dynamics have been illustrated with examples. This is no longer a popular method and thus, the author specifically mentions the advantages offered by this method in his concluding remarks. The accuracy of full-quantum calculations in predicting spectra of hydrogen molecular cation and its isotopic variants has been reviewed by Leach and Moss. The hydrogen molecular ion is simple in the sense that electron correlation is not of concern in this species and a full quantum calculation can be carried out. The authors have deliberately limited the scope of this article to hydrogen molecular ions and stressed on the accuracy required to reproduce experimental numbers. This article will perhaps help the specialists in the field to learn the details of such calculations. Another theoretical article in this volume deals with analysis of molecular spectra. The excellent review by Kellman about algebraic methods in analysing spectra will benefit a large number of experimentalists. He describes the standard spectroscopic Hamiltonian as well as the more recent Lie algebraic techniques for fitting a detailed excited state spectrum. The application of algebraic Hamiltonians to complex spectroscopic problems has great advantages for the numerical task of fitting a spectrum, in comparison with trying to fit the spectrum to a potential energy surface. We hope that experimental spectroscopists critically evaluate this advantage!

Femtosecond pulse shaping and optical control have been discussed by Kawashima, Wefers and Nelson. This is a highly technical article, but we suppose, it would be helpful to those who are interested in coherent excitation in a short time-scale! Impulsive stimulated Raman scattering studies of coherent lattice vibrations in the solid state and impulsive one-photon absorption in atomic vapour have been discussed. Efficient photoinduced electron transfer in supramolecular and photosynthetic systems has been described by Franzen and Martin. They have included time-resolution of excited state vibrational motion, the electric field dependence of the quantum yield, and resonance Raman
and hole-burning experiments that probe the nature of the initially prepared excited state.

Laser cooling of neutral atoms to form a bound dimer between two free atoms has been discussed by Lett, Julienne and Philips. This branch of high resolution molecular spectroscopy has made significant progress in the past few years and this article will be a good starting point for a newcomer in the field.

With the recent development of zero-kinetic energy (ZEKE) photoelectron spectroscopy as well as resonance enhanced multiphoton ionization (REMPI) sub-wavelength resolution in photoelectron spectroscopy are routinely achievable and there have been numerous reports of rotationally resolved photoelectron spectra of light molecules. Wang and McKoy review the theoretical framework to understand the experimental results. Central to the understanding of the rich dynamics of rotational quantum state specific studies of molecular photoionization are a number of dynamical issues such as strong l-mixing in the molecular photoelectron continua, parity selection rules, partial wave mixing and interference. The article also reviews the experimental results of the rotational resolved PES of a number of small molecules.

The infrared reflections absorption spectroscopy (IRRAS) technique is now no longer restricted to the study of well defined surfaces and more complex systems are being studied by this technique. IRRAS has been applied to investigate monolayers formation at the air–water interface. Mendelsohn, Brauner and Gericke review both the experimental and theoretical status of the field. Based on their survey the authors predict that the time is ripe for additional application of IRRAS especially to biological problems — interfacial enzyme catalysis, pulmonary surfactant functions, etc.

While experimental surface chemistry is moving towards an era where more complex systems are being studied, theoretical models still have a long way to go. While there are numerous reports on theoretical and computational investigations of adsorption of small molecules on well-defined surfaces, concomitant studies on the reactions of these adsorbed molecules have been few and far apart. This is partly because microscopic simulations, classical molecular dynamics or quantum scattering, require accurate potential energy surfaces. Garrison and Srivastava have reviewed the various recipes for generating many body reactive potential energy surfaces as well as their application. The potential energy surfaces described are for specific systems, the group IV elements and metals. The authors conclude by emphasizing the need for the development of new functional forms for multicomponent reactive systems.

Nuclear magnetic resonance continues to be an exciting technique for structure elucidation especially of biomolecules. In the last few years, an almost bewildering array of sophisticated new pulse experiments have been developed. Pelton and Wemmer describe the development of heteronuclear pulse sequencing experiments wherein the chemical shift of a proton is correlated with heteronuclear (14N, 13C or 31P) chemical shifts. The technique has allowed investigation of protein and nucleic acid structures in the 10-40 kDa range in contrast to homonuclear 1H methods which are limited to systems less than 10 kDa in size. Coulombic interactions and salt effects in nucleic acid solutions have been described in an article by Anderson and Thomas Record, Jr.

Nanotechnology is an emerging discipline within physical chemistry. Primary interest has focussed on the novel electronic structure and reactivity properties of small particles. Recent advances in the preparation and characterization of nanocrystals have also helped in addressing one of the long-standing questions of how large a system should be before it can exhibit a true thermodynamic phase transition. Any explanation or investigation would have to eliminate or establish the role of surface energy of these particles. The article on high pressure structural transformations in CdSe, CdS and Si nanocrystals by Tolbert and Alivisatos is quite timely. They review the experimental situation on solid–solid structural transformations in particles with different sizes and conclude that the observed elevation in the structural transition pressure is kinetic rather than a thermodynamic phenomenon.

In an excellent article, Yang and Parr describe various new developments in the density functional theory for calculating electronic structure of molecules. The goal of the article is set out clearly in the introduction. Recent contributions to the basic theory, extension of the applicability to very large molecules and the understanding of chemical reactivity have been considered for discussion. This article is timely since this field is seeing a tremendous recent surge in popularity among chemists. The accuracy achievable currently using this method has been compared with that of conventional quantum chemical calculations for computing ground states.

Nucleation plays a key role in many natural phenomena, from crystallization in melts to particle formation in stratospheric clouds. It is not surprising that the study of homogenous and heterogenous nucleation is an old subject. Recent developments in both theory and experiment have given rise to a resurgence of interest in nucleation. Experimentalists, today, can measure actual nucleation rates from 10^-4 to 10^5 cm^-3 s^-1 as well as probe the molecular content of these nucleating clusters using a variety of techniques. Experiments have gone hand-in-hand with progress in large-scale molecular dynamics simulation of the nucleation process. These developments have now made it possible to simulate both by experiment and computation, many of the particle formation phenomena occurring in the atmosphere. The article by Laaksonen, Taluquer and Oxtoby reviews all aspects of nucleation, experiment, theory and applications and provides a reasonable introduction to the subject for the non-initiate.

Finally, we have one criticism about the organization of this volume. No particular format has been followed by the authors while writing the reviews. As a result while some articles give a broad perspective of a field, others are narrow and limited in scope. All articles, however, carry important references in the field for the readers. This volume of Annual Review of Physical Chemistry certainly covers current topics and will be a useful addition to all libraries and groups working in the area of physical chemistry/chemical physics.

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