

PHOTOSELECTIVE CHEMISTRY

PART 1

Edited by

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ADVANCES IN CHEMICAL PHYSICS
VOLUME XLVII

Series editors

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PHOTOSELECTIVE CHEMISTRY

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ADVANCES IN CHEMICAL PHYSICS

VOLUME XLVII

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INTRODUCTION

Few of us can any longer keep up with the flood of scientific literature, even in specialized subfields. Any attempt to do more, and be broadly educated with respect to a large domain of science, has the appearance of tilting at windmills. Yet the synthesis of ideas drawn from different subjects into new, powerful, general concepts is as valuable as ever, and the desire to remain educated persists in all scientists. This series, *Advances in Chemical Physics*, is devoted to helping the reader obtain general information about a wide variety of topics in chemical physics, which field we interpret very broadly. Our intent is to have experts present comprehensive analyses of subjects of interest and to encourage the expression of individual points of view. We hope that this approach to the presentation of an overview of a subject will both stimulate new research and serve as a personalized learning text for beginners in a field.

ILYA PRIGOGINE
STUART A. RICE

PREFACE

Photoselective chemistry is concerned with the influence of selective optical excitation on the acquisition, storage, and disposal of energy and on the reactivity of molecules, in both gaseous and condensed phases. The very considerable recent progress in this field is largely due to the introduction of lasers, both as pumping and as probing devices, and to the intense theoretical effort stimulated by the many new and intriguing experimental findings. Photoselective chemistry is an interdisciplinary research area, blending concepts and techniques from a wide variety of fields. The articles assembled in these volumes describe many of the theoretical and experimental results now in hand, with the goal of contributing to the synthesis of a conceptual framework with which one can understand a broad spectrum of photophysical and chemical processes. The field is too young, and too little is known, to permit compilation of a definitive treatise. Instead, the contributions in these volumes reflect our opinion of the kinds of information that must be accumulated before it is possible to develop an integrated approach to the interpretation of observations already made and to the development and exploitation of these for new approaches to photochemistry. The same (opinionated) point of view guided the Organizing Committee [J. Jortner (Chairman), S. Kimel, A. Levin, R. D. Levine] of the Laser Chemistry Conference, which took place on December 15–22, 1979 at Ein Bokek, Israel, under the auspices of the National Council for Research and Development, Jerusalem, Israel. Indeed the decision to compile these volumes was triggered by the intensive and exhaustive problem-oriented discussions that took place during that Conference. In addition to contributions by participants at the Ein Bokek meeting, we have included many others, the overall goal being to provide an up-to-date set of authoritative reviews spanning the various aspects of photoselective chemistry.

The first article is meant to serve as an introduction to the entire field; it provides an overview of the relevant concepts, problems, ideas, and experiments described in the following papers. This introductory article was written after receipt of the other contributions so that cross-references could be made. The following articles have been organized in topical groups. Where it was desirable and practical, an introductory article to the given topic is placed first. The general organization of the material is

as follows:

1. Aspects of Intramolecular Dynamics
2. Multiphoton Induced Chemistry
3. Studies of Collision Effects
4. Studies in Condensed Media
5. Other Aspects of Photoselective Chemistry

We have followed the general policy of the *Advances in Chemical Physics* in that the authors have been given complete freedom, our point of view being that the person who pioneered the topic is the best judge of the appropriate mode for its presentation. We believe that the results have more than vindicated our approach and hope that the reader concurs. These volumes offer the newcomer a review of the entire field, yet in each and every direction reach the forefront of the current research effort and even attempt to explore the perspectives and future of photoselective chemistry.

We are grateful to the participants of the Ein Bokek Conference and to numerous colleagues and friends, whose lively and probing discussions convinced us of the merits of this project, and to the staff of Wiley-Interscience for welcoming and supporting it. We thank the authors for their willingness to contribute to this endeavor and for their adherence to a timetable, which enabled us to send the manuscripts to the publisher in the Fall of 1979. The wide range of subjects touched on in these volumes bears witness to the scope of photoselective chemistry and to the contagious enthusiasm of its practitioners.

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January 1981

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CONTENTS

PHOTOSELECTIVE CHEMISTRY <i>By Joshua Jortner and R. D. Levine</i>	1
Section 1. Aspects of Intramolecular Dynamics	115
AN OVERVIEW OF THE DYNAMICS OF INTRAMOLECULAR TRANSFER OF VIBRATIONAL ENERGY <i>By Stuart A. Rice</i>	117
INTRAMOLECULAR ENERGY TRANSFER: THEORIES FOR THE ONSET OF STATISTICAL BEHAVIOR <i>By Paul Brumer</i>	201
THE INFORMATION THEORETIC APPROACH TO INTRAMOLECULAR DYNAMICS <i>By R. D. Levine</i>	239
BOND MODES <i>By Martin L. Sage and Joshua Jortner</i>	293
VAN DER WAALS MOLECULES <i>By Donald H. Levy</i>	323
INTRAMOLECULAR DYNAMICS OF VAN DER WAALS MOLECULES <i>By J. A. Beswick and Joshua Jortner</i>	363
Section 2. Multiphoton-Induced Chemistry	507
REDUCED EQUATIONS OF MOTION FOR COLLISIONLESS MOLECULAR MULTIPHOTON PROCESSES <i>By Shaul Mukamel</i>	509
N-LEVEL MULTIPLE RESONANCE <i>By Abraham Ben-Reuven and Yitzhak Rabin</i>	555
LASER EXCITATION OF SF ₆ : SPECTROSCOPY AND COHERENT PULSE PROPAGATION EFFECTS <i>By C. D. Cantrell, A. A. Makarov, and W. H. Louisell</i>	583

INITIATION OF ATOM-MOLECULE REACTIONS BY INFRARED MULTIPHOTON DISSOCIATION <i>By Paul L. Houston</i>	625
INFRARED LASER CHEMISTRY OF COMPLEX MOLECULES <i>By R. B. Hall, A. Kaldor, D. M. Cox, J. A. Horsley, P. Rabinowitz, G. M. Kramer, R. G. Bray, and E. T. Maas, Jr.</i>	639
LUMINESCENCE OF PARENT MOLECULE INDUCED BY MULTIPHOTON INFRARED EXCITATION <i>By Avigdor M. Ronn</i>	661
ELECTRONIC LUMINESCENCE RESULTING FROM INFRARED MULTIPLE PHOTON EXCITATION <i>By Hanna Reisler and Curt Wittig</i>	679
ELECTRONICALLY EXCITED FRAGMENTS FORMED BY UNIMOLECULAR MULTIPLE PHOTON DISSOCIATION <i>By Yehuda Haas</i>	713
Author Index	735
Subject Index	763

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ADVANCES IN CHEMICAL PHYSICS

VOLUME XLVII

PHOTOSELECTIVE CHEMISTRY*

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CONTENTS

I.	Prologue	2
	A. Energy Acquisition	2
	B. Energy Storage	9
	C. Energy Disposal	12
II.	Experimental Observables	13
	A. Time-Resolved Observables	13
	B. Energy-Resolved Observables	14
	C. Observables Pertaining to Coherent Optical Effects	15
III.	Intramolecular and Intermolecular Relaxation	16
IV.	Predissociation	19
V.	Nonreactive Molecular Processes	29
VI.	Electronic Relaxation	40
VII.	Inverse Electronic Relaxation	46
VIII.	Intramolecular Energy Flow	51
IX.	Unimolecular Reactions	56
X.	Collisional Processes	58
XI.	Coherent Optical Effects for Pedestrians	65
XII.	High-Order Multiphoton Molecular Processes	70
XIII.	Relaxation and Dephasing in Condensed Phases	82
XIV.	Multiphonon Processes	90
XV.	Digression on Biophysics	98
XVI.	Epilogue	102
	References	104

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I. PROLOGUE

Photoselective chemistry is the exploration of the consequences of selective optical excitation on the acquisition, storage, and disposal of energy in molecules and in condensed phases. The outstanding progress achieved in this field during the last decade stems from two directions. First, extensive and exhaustive theoretical studies in the area of intermolecular and intramolecular dynamics provided a conceptual framework for the general understanding of a variety of nonreactive and reactive molecular photophysical and chemical processes, thereby establishing a firm basis for the elucidation of the nature of energy storage and disposal on the molecular level.¹⁻¹⁷ Second, the advent of laser sources had a remarkable impact on experimental progress in the field.¹⁸⁻²² Although significant information on excited-state dynamics was obtained in the past utilizing conventional optical excitation sources, the introduction of laser sources surpassed and eclipsed previous experimental work in providing new ways and means for energy acquisition as well as in advancing novel methods for the interrogation of the basic processes of energy storage and disposal. The degree of detail currently available is such that methods for the compaction and correlation of the basic data have to be introduced.

Photoselective chemistry can be considered as a truly interdisciplinary field, providing blending and integration of modern experimental methods and of theoretical concepts for a wide spectrum of fields, such as radiation theory,¹⁵ quantum electronics,²³ scattering theory,²⁴ molecular spectroscopy,²⁵⁻²⁷ intramolecular dynamics,¹⁻¹⁷ as well as solid-state and condensed phase physics and chemistry.^{28, 29} A multitude of experimental and theoretical methods from all these areas has been adopted to unveil the nature of excited-state photophysical and photochemical processes. It is our opinion that the basic approach to the understanding of photoselective chemistry should be problem-oriented rather than technique-oriented, so that the variety of the new, sophisticated, and exciting experimental methods advanced in this field should be considered, as well as the elucidation of the basic microscopic processes. Accordingly, we shall proceed to discuss the many-faceted nature of energy acquisition, storage, and disposal in molecules and in condensed phases as experimentally investigated and as explored theoretically from a microscopic point of view.

A. Energy Acquisition

The aspect of energy acquisition pertains to the central feature of photoselective excitation, i.e., the "preparation" of well-defined "initial"

states by optical excitation.¹³⁻¹⁷ During the past decade lasers have been extensively utilized in this area, taking advantage of many of the unique features of these optical excitation sources, which will now briefly be considered.

1. *Spectral Range.* Currently, available lasers span a broad energy region from 10 eV to 0.1 eV. Typical sources include vacuum ultraviolet lasers in the range 8.0–9.2 eV operating by third harmonic generation in metallic vapors,³⁰ ultraviolet excimer lasers emitting at several energies in the range 6.3–4.0 eV,³¹⁻³³ ultraviolet and visible solid-state Neodymium glass and Ruby lasers together with their second and third harmonics,³⁴ ultraviolet and lasers based on second harmonic generation from dye lasers and visible lasers spanning the energy range of 6.0–1.5 eV,³⁴ as well as infrared laser sources such as chemical lasers³⁵ and the popular CO₂ laser at ~0.12 eV.³⁴

2. *Tunability.* Some laser sources can be tuned over quite a broad energy range. Vacuum ultraviolet lasers are currently tunable over a range of 9.2–8.0 eV.³⁰ A combination of a variety of ultraviolet and visible dye lasers and their second harmonic results in tunability over the broad range of 6.0–1.5 eV.³⁴ Tunability in the infrared is currently restricted to low-power narrow-range CW diode lasers.³⁶

3. *High Power.* The power output of some laser sources is remarkably high, e.g., 10^9 W cm⁻² for mode-locked Nd glass and Ruby lasers,^{19, 37} a power output of $\sim 10^{12}$ W cm⁻² being accomplished for the iodine near infrared laser,³⁸ while for infrared CO₂ laser the accessible power is 10^6 – 10^9 W cm⁻².³⁹⁻⁴³ High-power laser sources were utilized to achieve high-order electronic and vibrational multiphoton excitation in atoms, molecules, and solids. These unconventional excitation processes involve two- and three-photon excitation studies of molecular states,⁴⁴ high-order multiphoton atomic ionization,^{45, 46} and high-order molecular multiphoton vibrational excitation,⁴⁰⁻⁴³ fragmentation,³⁹⁻⁴³ isomerization,^{47, 48} and ionization.⁴⁹

4. *High Energy.* Photoselective excitation of extremely weak absorption bands can be accomplished by intracavity one-photon absorption, providing a novel way for the interrogation of chemical consequences of high vibrational excitations.⁴⁰⁻⁴³ High-order multiphoton excitation of very large molecules, such as S₂F₁₀⁵¹ or the esoteric molecule UO₂(hfacac)₂THF₃,^{52, 53} is determined by the laser energy fluence⁴⁰ and can be conducted using CW infrared lasers.^{52, 53}

5. *Ultrashort Duration.* The temporal duration of some pulses can be extremely short, that is, in the picosecond region. Mode-locked solid-state lasers in the visible deliver pulses in the time domain of 6–30 psec,^{19, 37} mode-locked dye lasers yield pulses in the range >1 –10 psec¹⁹ in the visible and near ultraviolet, while 30-psec pulses were obtained from an infrared CO₂ laser.⁵⁴ These ultrashort pulses provide a powerful tool for the interrogation of intramolecular and intermolecular dynamics on the picosecond time scale.

6. *Coherence Effects.* Single-mode laser sources can be utilized for excitation of molecular ensembles by $(\pi/2)$ or π optical pulses.^{55, 56} One can study the interesting process of driving of the system by an electromagnetic field, exploring coherent transient effects in electronically excited states, and interrogating the retention of phase coherence between the molecular ground state and the excited states.

Lasers have played a leading role as optical excitation sources in the energy range 10–0.1 eV. At higher energies above 10 eV, photoselective, tunable, energy-resolved, and time-resolved excitation can be accomplished using synchrotron radiation sources, which show great promise for the use in high-energy intramolecular dynamics.⁵⁷ We shall confine the present discussion to energy acquisition below 10 eV where the characteristics of lasers were utilized for energy-resolved and time-resolved excitation, for high-order multiphoton excitation as well as for establishing phase coherence between the excited state and the ground state in a variety of molecular and condensed-phase systems. Studies of intramolecular dynamics focus attention on nonradiative relaxation processes occurring in “isolated” collision-free molecules and how these intramolecular processes are affected by coupling between a molecule and an external medium. The systems utilized for the exploration of intramolecular dynamics of isolated molecules essentially involve molecules in the bulb, as well as molecules in the thermal beams and in supersonic beams, which will now be considered.

a. Molecules at low pressures. Optical excitation of molecules in the low-pressure gas phase can be conducted at pressure down to 10^{-3} – 10^{-4} torr, where the time between gas–kinetic collisions is 10^{-4} sec. Considerably higher collision cross-sections were reported, however, for rotational–vibrational relaxation in electronically–vibrationally or vibrationally excited states. For example, the cross-section for collisional rotational relaxation of electronically excited benzene in the ${}^1B_{2u}$ state by a ground-state benzene molecule is 500 \AA^2 ,⁵⁸ while the cross-section for SF₆–SF₆ collision involving a vibrationally excited molecule is 300 \AA^2 .⁵⁹ Thus, in bulb experiments collision-free conditions at 10^{-3} torr can be accomplished on

a time scale of $\sim 10^{-5}$ sec, and the excited-state intramolecular dynamic process can be considered to occur in the "isolated" molecule which is collision-free on the time scale of microseconds, or so. Such bulb experiments led to pertinent information on electronic relaxation in electronically-vibrationally excited states of large "isolated" molecules⁹⁻¹⁷ and were crucial in establishing the features of collisionless, multiphoton molecular photofragmentation and isomerization on the ground-state potential surface.⁴⁰⁻⁴³

b. Molecules in thermal molecular beams. To accomplish electronic and/or vibrational excitation of an "isolated" collision-free molecule, a laser beam was crossed with an effusive, thermal, molecular beam.^{60, 61} The intramolecular dynamics in the first electronically excited singlet state of several large molecules, i.e., pentacene and benzophenone, were investigated in thermal beams.^{60, 61} Studies of multiphoton molecular photofragmentation in beams established the collisionless nature of this class of phenomena and contributed to the understanding of the decomposition mechanism by the determination of the translational energy of the fragments.^{62, 63} The intrinsic limitation of probing the consequences of laser excitation of large molecules in thermal molecular beams is due to thermal inhomogeneous broadening effects (TIB), that is, thermal rotational broadening and vibrational sequence congestion (see Table I), which preclude truly photoselective excitation of an ensemble of large molecules at room temperature.

c. Molecules in supersonic beams. A powerful way to overcome TIB effects rests on the use of isentropic-nozzle beam expansions. The low translational, rotational, and vibrational temperatures achieved in supersonic-free expansions are sufficient to eliminate all rotational broadening effects in small molecules, and to avoid all vibrational sequence congestion effects in large molecules. The use of seeded molecular beams provides a novel experimental approach for genuine photoselective excitation of large

TABLE I
Origins of Inhomogeneous Broadening

Systems	Conserved Quantity	Type of Inhomogeneous Broadening
Isolated molecules	Linear momentum Angular momentum Vibrational state	Doppler Rotational Sequence congestion
Medium-perturbed molecules	Electronic-vibrational state	Site splitting and statistical distribution of trapping sites

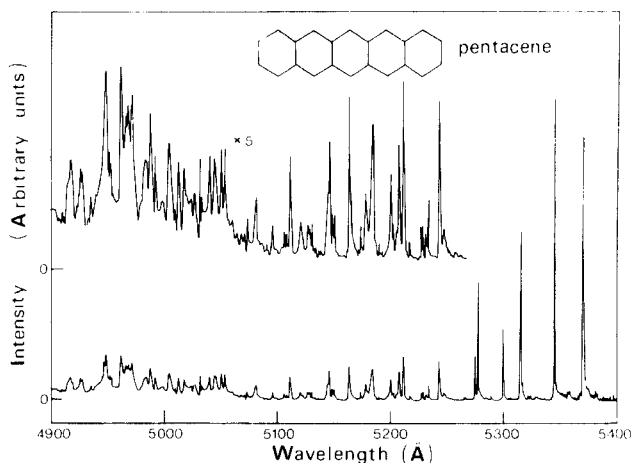


Fig. 1. Fluorescence excitation spectrum of gas-phase isolated pentacene ($C_{22}H_{14}$) molecule cooled in a supersonic expansion. The data are reproduced from the work of Amirav, Even, and Jortner (Ref. 76). Pentacene (at pressure of 5×10^{-2} torr) was seeded into Ar and expanded from a pressure of 210 torr through a $150\text{-}\mu\text{m}$ nozzle. The exciting dye laser (spectral bandwidth 0.3 cm^{-1}) crossed the supersonic beam at 5 mm down the nozzle. The wavelength scale corresponds to that of the laser. The intensity scale monitors the total fluorescence, normalized to the laser intensity. The fluorescence excitation spectrum in the range 5400–4900 Å was assigned⁷⁶ to the $S_0(^1A_{1g}) \rightarrow S_1(^1B_{2u})$ transition, the electronic origin being located at 5368 Å.

molecules.^{64–69} As is evident from Figs. 1 and 2 laser spectroscopy of large molecules seeded in supersonic beams allows for an increase of spectral resolution of about three orders of magnitude over that possible with room-temperature bulb experiments. The dynamics of several isolated “ultracold” large molecules, such as formaldehyde,⁷⁰ benzene,⁷¹ naphthalene,^{72, 73} phthalocyanine,⁷⁴ tetracene,^{69, 75} pentacene,^{75, 76} and ovalene,⁷⁷ in their lowest excited singlet states in a supersonic beam, provided central information on interstate electronic relaxation and on intrastate vibrational energy redistribution in excited states of large molecules. Not only conventional molecules can be excited in supersonic beams but supersonic-free expansion has also been extensively and fruitfully utilized to prepare a wide variety of weakly bound van der Waals molecules^{66, 67} (Chapter 5), whose intramolecular dynamics is of considerable interest.

We shall now proceed to consider the basic systems which were explored in the context of medium-perturbed, intramolecular dynamics and non-radiative relaxation processes in condensed phases:

d. Selective collisional effects. Collisional effects have constantly plagued the experimentalists engaged in studies of intramolecular dy-

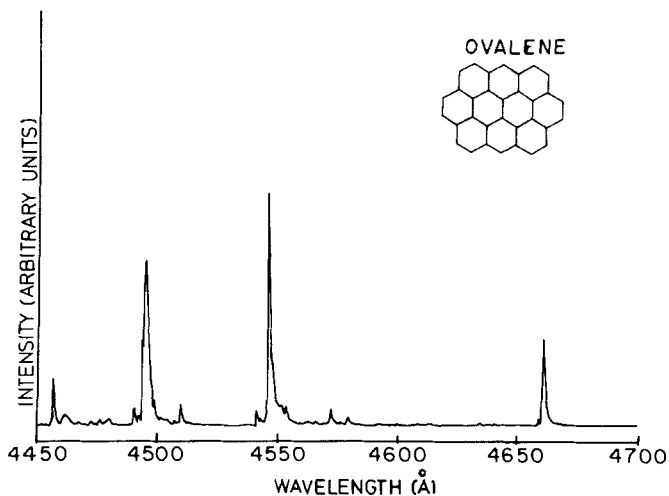


Fig. 2. Fluorescence excitation spectrum of the ovalene ($C_{32}H_{14}$) molecule cooled in a supersonic expansion. These data are reproduced from the work of Amirav, Even, and Jortner (Ref. 77). Ovalene (at pressure of 5×10^{-2} torr) was seeded at Ar and expanded through a 200- μ m ceramic nozzle. Experimental conditions similar to that of Fig. 1. The excitation spectrum in the range 4700–4450 Å corresponds⁷⁷ to the $S_0(^1A_{1g}) \rightarrow S_1(^1B_{3u})$, the lowest energy spectral feature at 4662 Å being attributed to the electronic origin.

namics in “isolated” molecules. It is extremely important to understand the interplay between intramolecular dynamics and intermolecular perturbations. In this context one should attempt to extract microscopic information regarding the selective effects of collisions, which was obtained from energy-resolved emission studies from electronically excited states of collisionally perturbed large molecules (“Collision Induced Intramolecular Energy Transfer in Electronically Excited Polyatomic Molecules,” Chapter 23). The thermal distribution of the energies of the colliding molecules limits the information content emerging from such experiments. The ultimate goal in this area will be the exploration of the consequences of monoenergetic collisions on intramolecular dynamics. Significant progress in that direction was accomplished recently (Chapter 23) by exploiting some features of supersonic beam expansions, which made it possible to study energy-resolved collisional effects in the proximity of the nozzle source.^{78, 79} Other recent studies are discussed in Chapters 22–26.

e. Matrices and Mixed Crystals. A traditional way to eliminate TIB effects in the spectroscopy of large molecules involves the study of low concentration guest molecules in a low-temperature solid, glass, or in a mixed crystal. Even at low temperatures the effects of phonon broadening, manifested in the appearance of multiphonon side bands, can be severe in

spreading the intensity of the vibronic molecular state over a wide energy range. These phonon-broadening effects can be reduced by a proper choice of the host, so that the molecule–lattice nuclear equilibrium configurations are not distorted on electronic excitation and the zero-phonon lines dominate the spectrum, as in the case for Shpolskii matrices⁸⁰ and for some mixed organic crystals.⁸¹ Even in such favorable systems site-splitting effects are exhibited, and each of the zero-phonon lines is severely broadened due to the statistical distribution of trapping sites, i.e., intrinsic inhomogeneous broadening effects. A visual demonstration of such complications is presented in Fig. 3. Spectroscopic studies of zero-phonon lines

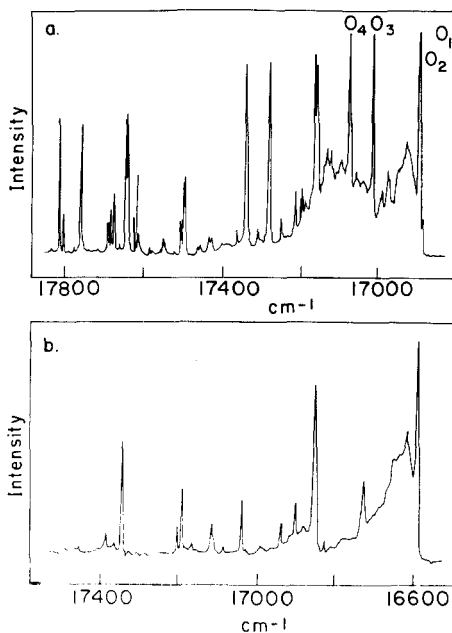


Fig. 3. Absorption spectrum of the pentacene molecule in host molecular crystals at 1.4 K. These data are reproduced from the work of Lambert and Zewail³³⁴ (a) Pentacene in *p*-terphenyl host. (b) Pentacene in naphthalene host. These low-temperature guest spectra reflect sharp features corresponding to zero-phonon lines (ZPO) of the vibrational transitions of the $S_0 \rightarrow S_1$ electronic excitation. The lowest energy ZPO corresponds to the electronic origin. Four complications inherent in these spectra are evident: (1) Site splitting. The features O_1 , O_2 , O_3 and O_4 of pentacene/*p*-terphenyl correspond to different trapping sites. (2) Lattice phonon excitation. The broad absorption on the high energy side of each ZPO reflect excitation of lattice phonons, induced by molecule–lattice coupling. (3) Inhomogeneous broadening. The width of the lowest ZPO originates from a statistical distribution of trapping sites. (4) Vibrational relaxation. The broadening of some of the ZPOs corresponding to vibrationally excited states has a large contribution from medium-induced vibrational relaxation, cf. Section XIII.

provide useful data regarding the energetics of electronically–vibrationally molecular excitations. Unfortunately, such studies of matrix isolated molecules provide only very limited information regarding intramolecular dynamics, as selective excitation of vibrationally excited molecular states results in medium-induced vibrational relaxation, which masks the intramolecular effects. Nevertheless, some useful information regarding intramolecular dynamics in the vibrationless electronic origin of an electronically excited state of a molecule in a low-temperature glass or crystal can be obtained.

f. Solutions. Studies of excited state dynamics of molecules in solutions provide a traditional research area in physical chemistry. The interpretation of the rich and diverse information regarding excited-state dynamics of molecules in solution, usually conducted at room temperature, is complicated due to TIB effects, phonon broadening, as well as severe inhomogeneous broadening effects. Of particular interest are dynamic processes in dense polar and also in nonpolar fluids, which are specific to the liquid phase. These can be grouped into excited-state or ground-state processes. In the first category we shall consider excited-state chemical processes, such as intermolecular and intramolecular proton transfer in polar solvents (“Laser Studies of Proton Transfer,” Chapter 33), which provide interesting information regarding the dynamics of electronically excited states.⁸² In the second category we shall mention the interesting process of the dynamics of the localization of an excess electron in polar solvents⁸³ (“Picosecond Dynamics of Electron Relaxation Processes in Liquids,” Chapter 30), which utilizes the excess electron, produced by photoionization of a guest molecule or ion in solution, as a probe for the local and the long-range structure in liquids.

g. Biological systems. Photoselective chemistry is expected to provide fundamental contributions toward the elucidation of some of the basic phenomena in photobiology,⁸⁴ unveiling the basic mechanism of photosynthesis⁸⁵ and of the vision processes⁸⁶ (Chapter 32). During the last few years several studies on model systems of the photosynthetic systems^{87–90} and of rhodopsin⁹¹ were performed, as well as investigation of the chemical and biochemical consequences of photoselective excitation of systems *in vitro* was conducted. The utilization of photoselective ultrafast excitation at room temperature, as well as low temperature systems,^{86, 92} is expected to provide a fruitful blending between the techniques and the concepts of chemistry, photophysics, photobiology, and biophysics.

B. Energy Storage

The problem of energy storage pertains to the basic aspects of intramolecular and intermolecular dynamics of “isolated” molecules, of col-

tionally perturbed molecules and of molecules in condensed phases. A systematic description of dynamic processes should address the following three aspects.

1. *Characterization of the molecular level structure.* Excited-state level structure in vibrationally–electronically excited states of molecules may include:
 - a. Sparse bound level structure in diatomics, in small polyatomics, as well as in some low-lying vibrationally excited states of large molecules.
 - b. An intramolecular quasicontinuum consisting of a dense vibrational manifold of bound vibronic levels, which is characterized by a high density of states.
 - c. Dissociative continua consisting of unbound states of the fragments.
 - d. Ionization continua corresponding to unbound electron-positive ion pairs.

The molecular structure is specified in terms of the eigenstates of the entire molecular (nuclear–electronic) Hamiltonian for the system. There is a basic physical distinction between bound level structures, such as *a* and *b*, where the molecular electronic–nuclear states are localized, and a continuous spectrum, where the electronic–nuclear states are extended. Above the onset of the lowest-lying dissociative or ionization continuum, the molecular states correspond to extended levels. There can be no peaceful coexistence between bound and continuous states above the onset of the lowest-lying continuum. When resonances are exhibited in the continuous spectrum, the relevant molecular states can be described in terms of a superposition of discrete and continuum states. However, a finite contribution from continuum states will always prevail above the onset.

2. *Characterization of the excitation amplitudes.* The energetic spread of the transition moments connecting the ground state of lower-lying states with the excited-state level structure determines the accessibility of these excited states to optical excitation. The distribution of the transition moments between the molecular eigenstates of the total Hamiltonian is expected to exhibit sharp structure in range *a*, to show a quasicontinuous structure characterized by resonances in range *b* and to reveal a smooth distribution with some superimposed resonances in ranges *c* and *d*. We note in passing that the characterization of the excitation amplitudes is more general than the specification of the distribution of the oscillator strengths, as it makes possible the description of interference effects. The resonance structure and the

interference effects exhibited in congested and in continuous spectra can adequately be described in terms of zero-order states, a problem of considerable technical importance which will subsequently be considered in Sections V and VII. What is important for the purpose of the present general discussion is that the distribution of the transition amplitudes to the molecular eigenstates determines accessibility and photoselectivity by optical excitation.

3. *Specification of the initial conditions.* A variety of excitation methods can be applied to molecular systems, e.g., short-time excitation, energy-resolved excitation, high-power multiphoton excitation, a coherent excitation, just to mention a few examples. It has been realized since the early days of quantum mechanics, and is now well established in the area of chemical physics, that a stationary state of the molecular Hamiltonian exhibits only radiative decay, and that only nonstationary states of the molecular Hamiltonian are metastable with respect to intramolecular dynamics. The metastable molecular states "prepared" by an optical excitation are determined by the excited-state level structure, by the energetic spread of the transition amplitude, as well as by the energetic temporal intensity and coherence properties of the excitation light source. Thus, the excitation conditions govern the subsequent dynamic time evolution of a molecular system. We can conclude that the intramolecular dynamics of a given system provide the signature of the initial conditions.

Information concerning excited-state level structure is provided by the well-established discipline of molecular spectroscopy. Basic data concerning vibrational level structure on the ground-state potential surface, important for the understanding of multiphoton excitation⁴⁰⁻⁴³ were obtained from high-resolution infrared spectroscopy,⁴¹ while laser spectroscopy of large molecules in supersonic beams lead to interesting data regarding sparse and quasicontinuous bound molecular level structure in low-lying electronic states.^{69, 76} Spectroscopic data also provide information on the distribution of the transition amplitudes. Conventional spectroscopy establishes the energy distribution of the oscillator strength from the ground vibrational-electronic state to excited states. Low resolution spectroscopy of vibrationally excited molecules⁹³ yield important information regarding the distribution of intensity between highly excited states, which is crucial for the understanding of high-order multiphoton vibrational excitation.

The basic information concerning energy storage should address the question of the mechanisms of intramolecular energy exchange and the time scales for such processes.

C. Energy Disposal

The problem of energy disposal is concerned with the basic microscopic mechanisms of the damping of the excitation energy. It should be borne in mind that the radiative decay channel provides just one possible energy decay route and that a variety of alternative energy disposal mechanisms should be considered. Exploration of the energy disposal phenomena requires the interrogation of the decay channels. This information essentially involves the determination of all possible cross-sections but has to be singled out in view of its primary chemical significance.

1. Identification of reactive and nonreactive channels in molecular systems. This is a simple matter in diatomics but becomes a rather difficult and important task with increasing size of the molecule.
2. Specification of reactive and nonreactive channels in condensed phases. Here the media affect the intramolecular processes and, in addition, new intramolecular and/or intermolecular electronic and vibrational energy transfers have to be considered.
3. Determination of branching ratios between various parallel channels.
4. Characterization of parallel and consecutive decay channels.
5. Investigation of possible interference effects between different channels.
6. Determination of internal energy (electronic, vibrational, rotational) content of the fragments.

Laser sources in conjunction with modern spectroscopic techniques have been extremely useful for the investigation of decay channels. Some of the modern techniques are:

1. Doppler spectroscopy of fragments ("Doppler Spectroscopy of Photo-fragments," Chapter 20).
2. Fluorescence of fragments resulting from one-photon excitation⁹⁴ Chapter 19 and from multiphoton excitation^{95, 96} (Chapters 12–14).
3. Laser spectroscopy of highly excited vibrational states reached by multiphoton excitation, (Chapter 7–9).
4. Laser spectroscopy of fragments.⁹⁷ ("Laser Diagnostics of Reaction Product Energy Distributions," Chapter 19).
5. Double resonance techniques.⁹⁸
6. Identification of products by conventional chemical techniques, such as gas chromatography and mass spectrometry.⁶²
7. Identification of products by laser spectroscopy⁹⁷ (Chapter 19).
8. Identification of products by spectroscopic methods, such as resonance Raman or CARS.⁹⁹
9. Studies of isotope separation resulting from multiphoton excitation,⁴² (and "Infrared Laser Chemistry of Complex Molecules," Chapter 11).

Lasers have also been extensively employed (Chapters 10, 15–17) to generate reactive excited states and radicals.

This brief introduction has been concerned with some aspects of the basic physical and chemical phenomena of acquisition, storage, and disposal of energy, with a special emphasis on the role of laser photoselective excitation in energy acquisition and on the interrogation of the rise and fall of excited molecular and condensed-phase excited states. It is the purpose of this chapter to serve as an overview of the problems, concepts, experiments, and ideas described in the present volumes. The prominence of the microscopic point of view in the description of excited-state dynamics, which is emphasized in the present and in the following chapters, reflects the blending between the development of theoretical concepts and of sophisticated experimental methods and provides a firm conceptual framework for the understanding of intramolecular and intermolecular dynamics. It is our goal to expose the present state of the art in this field and to explore the perspectives and future of photoselective chemistry.

II. EXPERIMENTAL OBSERVABLES

We shall first proceed to examine the experimental information pertaining to various aspects of energy acquisition, storage, and disposal. This will provide background for the subsequent discussion of the conceptual framework for the rationalization and interpretation of many of these diverse phenomena.

The basic information concerning intramolecular and intermolecular nonradiative relaxation dynamics in molecules and in condensed phases emerges from the following general classes of experimental observables.

A. Time-Resolved Observables

Direct information regarding the temporal decay of excited states is obtained from:

1. Monitoring radiative decay by time-resolved photon counting.
2. Monitoring populations of reactive and nonreactive decay channels by time-resolved absorption methods.

This direct information on the rise and fall of rotational–vibrational–electronic molecular states and vibrational–electronic excitations in condensed phases can be classified according to their different decay modes:

1. *Exponential decay.* This is the common decay mode, which was well documented in the low-energy (say, below 5 eV) range, and which corresponds to the decay times of metastable states and to the rates of population of all decay channels.

2. *Nonexponential decay.* This consists of a superposition of exponentials. Such effects may originate from two sources:
 - a. Inhomogeneous broadening of molecular states (Table I), which results in excitation of an incoherent superposition of states, and whose independent decay may be characterized by a distribution of lifetimes. These effects complicate the elucidation of the intrinsic dynamics.
 - b. Genuine intramolecular effects originating from intrastate and interstate intramolecular coupling may give rise to such interesting intrinsic effects.^{16, 100, 101}
3. *Quantum beats in the decay.* Such a pattern originates from interference effects between closely-lying excited levels.¹⁰² These interesting manifestations of interrelationships between the phases of excited states were reported for externally perturbed (Zeeman and Stark shifted) levels of atoms and diatomics. The more interesting situation of coherent decay of closely spaced indistinguishable closely lying states of polyatomic molecules resulting from mixing between two electronic configurations was not yet experimentally explored. A recent study¹⁰³ has reported the observation of molecular quantum beats in the decay of the singlet manifold of biacetyl, which is scrambled with the triplet background manifold, so that coherent effects can be exhibited by closely spaced singlet-triplet molecular eigenstates.

B. Energy-Resolved Observables

A variety of cross-sections for optical absorption, photon scattering, etc., yield basic data regarding reactive and nonreactive molecular processes. These studies sacrifice the time resolution for the sake of energy resolution, providing a blending of spectroscopic data with basic information concerning intramolecular dynamics. These observables are:

1. *Absorption cross-sections.* In the case of a simple isolated resonance in reactive and nonreactive processes, the homogeneous width of the Lorentzian line shape is determined by the decay rate of the metastable state. In more complex situations, when the background manifold, i.e., the continuum or the quasicontinuum, carries oscillator strength from the ground-state, Fano-type interference effects in absorption will be exhibited.¹⁰⁴⁻¹⁰⁶ Finally, interference effects in absorption to overlapping resonances¹⁰⁷ provide interesting information on interstate and intrastate coupling, which is complementary to that which will be obtained from time-resolved quantum beat experiments.
2. *Photon-scattering cross-sections.* These involve conventional off-resonance fluorescence and Raman scattering,¹⁰⁸ near-resonance

Raman scattering from dissociative continua and from ionization continua.¹⁰⁹⁻¹¹¹ The information obtained is complementary to but not identical with that obtained from absorption data.

3. *Cross-sections for population of reactive and nonreactive decay channels.* The modern techniques of picosecond spectroscopy in absorption and in emission, both in the ultraviolet, visible, and infrared regions¹⁹ have been extremely useful in this context.
4. *Angular distribution of products, i.e., neutral fragments and/or ions, resulting from excitation by polarized radiation.*¹¹²⁻¹¹⁴ For direct molecular ionization and dissociation processes, such experiments provide spectroscopic evidence concerning spatial orientation of optical transition moments in polyatomic molecules. For indirect reactive processes, such as autoionization and predissociation, the lifetimes of metastable states can be extracted from the angular distribution.¹¹⁴

C. Observables Pertaining to Coherent Optical Effects

Optical excitation by coherent light pulses can establish definite phase relationships between the ground-state and excited doorway states.¹¹⁵⁻¹²⁹ The temporal persistence of the phase relationships can be interrogated by studies of optical nutation, free-induction decay, and photon-echo experiments. These phase relationships are destroyed by dephasing phenomena, which are of three distinct types. First, intramolecular dephasing in reactive processes is equivalent to T_1 level depletion processes. Second, intramolecular dephasing in interstate and intrastate nonreactive relaxation in large isolated molecules and can be regarded as intramolecular T_2 processes.^{130, 131} Third, erosion of phase coherence by medium perturbations provide important chemical and physical information on intermolecular T_2 processes, which pertain to the consequences of the coupling of excited molecular states with the host medium.⁵⁶ Most of the coherent effects in the optical region have been limited to two-level systems.⁵⁵ The studies of retention of phase relationships in multilevel systems¹³²⁻¹³⁴ will be of considerable interest for the elucidation of multiphoton excitation of large molecules.

From the point of view of general methodology, the basic physical and chemical information emerging from the experimental observables falls into two broad classes:

- I. *Populations of individual excited states and/or populations of discrete (quasicontinuum) or continuous decay channels.* Temporal and energy-resolved information is obtained from some of the time-resolved and energy-resolved observables. This information regarding the population of excited and ground electronic-vibrational-rotational states of

the parent molecule and/or the fragments is of central chemical importance.

- II. *Phase relationships.* Information on phase relationships between excited states is obtained from the analysis of interference effect exhibited in the time-resolved observables and in the energy-resolved variables. Phase relationships between the ground and excited doorway states can be monitored by studies of coherence effects.

The major goal of the experimental and theoretical studies in the area of intramolecular and intermolecular dynamics is twofold. First, one has to elucidate the nature of the various intermolecular and intramolecular decay channels, the interaction between channels and the sequence of photo-physical reactive and nonreactive processes in excited states. Second, the consequences of phase relationships between excited states, as well as between the ground state and the excited doorway state, have to be explored in order to understand intramolecular interference effects, intramolecular dynamical processes and medium perturbations on excited states.

III. INTRAMOLECULAR AND INTERMOLECULAR RELAXATION

An outstanding goal of research in the area of molecular and condensed phase excited-state dynamics is the elucidation of a wide class of radiationless processes involving a large variety of intermolecular and intramolecular phenomena, such as electronic-vibrational exchange, (Chapter 26) vibrational-vibrational exchange, (Chapter 22) dissociation (and ionization) in direct processes and in the form of indirect processes, that is, predissociation and autoionization, as well as more complex chemical phenomena. These intramolecular and intermolecular processes can be classified as follows in the order of increasing complexity of the system involved:

1. Basic molecular processes.
2. Complex molecular processes.
3. Relaxation processes in external electric and magnetic fields.
4. Relaxation in intense electromagnetic fields.
5. Medium-induced processes.
6. Relaxation in condensed phases.

The basic intramolecular relaxation (Table II) processes fall into two distinct classes:

1. *Reactive processes*, e.g., autoionization¹³⁵ and predissociation,^{25, 27} which result in ionization or fragmentation.

TABLE II
Classification of Basic Intramolecular Relaxation Processes

Nature of decay channel	Nature of Coupling	
	Intrastate (1 electronic configuration)	Interstate (2 electronic configurations)
Reactive	Rotational predissociation	Autoionization
	Vibrational predissociation	Electronic predissociation
Nonreactive	Intramolecular vibrational energy redistribution in large molecules	Electronic relaxation (internal conversion and intersystem crossing) in large molecules

2. *Nonreactive processes*, e.g., intramolecular electronic relaxation⁷⁻¹⁷ and intramolecular vibrational redistribution¹⁴ in large molecules.

Another useful classification of the basic molecular processes separates those (intrastate) processes occurring on a single electronic potential surface from the (interstate) processes involving at least two distinct electronic configurations:

1. Intrastate dynamics involving some forms of rotational predissociation, as well as intramolecular vibrational energy redistribution which occurs between bound vibrational levels of large molecules.
2. Interstate dynamics incorporating the processes of autoionization, electronic predissociation, as well as electronic relaxation, i.e., internal conversion and intersystem crossing between bound states of large molecules.

The basic molecular processes we have been concerned with provide the framework for the elucidation of the nature of a variety of interesting chemical phenomena. Complex chemical processes in large molecules can be described in terms of several parallel and/or sequential basic molecular relaxation processes. While molecular photofragmentation of diatomic molecules involves just direct photodissociation or predissociation, the photofragmentation process becomes more complex with increasing size of the molecule. For triatomic molecules the effects of coupling various dissociative channels, that is, final-state interactions,¹³⁶ and effects of intramolecular energy exchange have to be incorporated. For the case of molecular photofragmentation of large polyatomic molecules one should

consider electronic relaxation, intramolecular vibrational energy redistribution, as well as vibrational predissociation and electronic predissociation. Photochemical rearrangements, such as isomerizations of large molecules,¹³⁷ involve contributions from a variety of basic processes, for example, electronic relaxation and intramolecular vibrational energy redistribution, and may also be strongly influenced by medium-induced steric hindrances and vibrational relaxation. The elucidation of the variety of decay channels contributing to these complex processes will provide firm grounds for the understanding of molecular photochemistry and radiation chemistry from a unified point of view.

Some of the intramolecular processes we have just considered can be affected by external fields. Control of intramolecular dynamics by external fields is of considerable interest, as such effects will provide a new variable to probe dynamic molecular processes. Little is presently known concerning the effects of external magnetic and electric fields on molecular relaxation processes. Only the effect of the magnetic field on some cases of electronic predissociation of diatomics, where the Zeeman term enhances the predissociation rate, is well documented.¹³⁸ The effects of external fields on nonreactive electronic relaxation have not yet been explored.¹³⁹ Another interesting feature of the effects of external fields involves field-induced decay processes, such as the ionization of highly excited atomic and molecular Rydberg states in intense electric fields.¹⁴⁰ This effect is of interest in relation to high-order multiphoton ionization.

Of considerable current interest are the consequences of radiative coupling with intense electromagnetic fields on molecular and condensed phase dynamics. Problems of intramolecular dynamics in intense radiation fields fall into two major categories:

1. Effects of intense fields on energy acquisition, as is the case of multiphoton atomic and molecular ionization,^{45, 46} as well as multiphoton molecular photodissociation and isomerization.³⁹⁻⁴³
2. Effects of intense fields on energy storage and disposal, which is exhibited in the novel and interesting field of radiative collisions^{141, 142} and electronic energy transfer induced by intense radiation fields.¹⁴³

Up to this point we were concerned with intramolecular dynamics in isolated molecules. The effects of medium perturbations on intermolecular and intramolecular dynamics are of importance in the understanding of the effects of collision-induced processes and medium perturbations in excited state reactivity in condensed phases. Collisional processes can be explored on the microscopic level by considering the role of van der Waals bonding on vibrational predissociation,¹⁴⁴ which results in vibrational relaxation.¹⁴⁵ The induction of collision-induced electronic relaxation¹⁴⁶

can be investigated by a similar approach. Turning now to some relaxation phenomena in condensed phases, we shall briefly consider separately intermolecular and intramolecular processes. Intermolecular processes involve electron transfer¹⁴⁸⁻¹⁵⁰ from ground-state or electronically excited states, electron-hole recombination in semiconductors¹⁵⁰ and in amorphous solids,¹⁵¹ group transfer processes,¹⁵² and intermolecular electronic energy transfer.^{153, 154} Intramolecular processes correspond to nonradiative electronic relaxation in ionic centers¹⁵⁵ and in insulators.¹⁵⁶ These processes can be described in terms of the decay of resonances, that is, metastable states of the entire system involving the reactive centers (electron or energy donor and electron or energy acceptor) coupled to the phonon field of the medium. One should notice the conceptual similarity between these phenomena and electronic relaxation in large molecules. The basic operative tools in the theory of intramolecular electronic relaxation phenomena in large molecules draws heavily on the concept of the weighted density of states, which bears a close analogy to the customary approach to elementary excitations in solids.

We shall now proceed to the discussion of intramolecular and intermolecular dynamics with an emphasis on the development of this field, not by defining it in the historical order but in the order of increasing complexity on the molecular level.

IV. PREDISSOCIATION

Unimolecular dissociation is the basic reactive process in an isolated, energy-rich molecule. In this section we pay particular attention to smaller molecules where the process is best described as one of predissociation.^{25, 27} For larger polyatomics, intramolecular energy migration plays an important role and needs to be discussed in the first instance (Sections V and VIII). We shall then return to unimolecular processes in Section IX.

It is convenient to classify the predissociation processes in accordance with which degrees of freedom undergo a change of state (are "non adiabatic") during the dissociation. The basic distinction is between interstate and intrastate processes, the latter taking place on a single electronic potential energy surface. The simplest example of interstate electronic predissociation is the decay of a metastable, discrete vibronic level to another, repulsive, electronic configuration. As early as 1927 Wentzel¹⁵⁷ used the quantum-mechanical time-dependent perturbation theory to derive the familiar expression for the decay rate, which is nowadays usually referred to as the Fermi golden rule.¹⁵⁸ With appropriate changes the same

expression applies to all other predissociation processes in which a change of state of any type takes place.

To describe the decay of an isolated metastable state n , it is convenient to assign to its energy ϵ_n an imaginary part

$$\epsilon_n = E_n - \frac{i\Gamma_n}{2} \quad (4.1)$$

The time-dependent part of the wavefunction, $\exp(-i\epsilon_n t/\hbar)$, is thus of diminishing amplitude. When excited, such a metastable state will exhibit a simple exponential decay, $|\exp(-i\epsilon_n t/\hbar)|^2 = \exp(-\Gamma_n t/\hbar)$ with a decay rate Γ_n/\hbar . It is the purpose of this section to identify the processes that give rise to a finite value of the "width" Γ_n and to examine the dependence of Γ_n on the relevant molecular parameters. We shall also comment on "inverse" predissociation or association processes which are important in recombination and other relaxation phenomena.

Intrastate processes cover the entire range from those where all degrees of freedom change adiabatically throughout to those where they are all strongly coupled. The latter are typical of thermally induced unimolecular processes in polyatomics, as discussed in Section IX. The simplest example of the former is rotational predissociation in diatomic molecules (Fig. 4). Consider a potential energy curve that can support bound states and where its long-range attractive part decreases typically as $C_6 R^{-6}$. For a finite value of orbital angular momentum J , the centrifugal barrier is repulsive and of longer range [$\hbar^2 J(J+1)R^{-2}$]. The resulting potential has a hump that can trap the system in the region of the well. Escape is by tunneling through the hump. The required theory in connection with α decay in nuclei was developed earlier by Condon and Gurney¹⁵⁹ and by Gamow.¹⁶⁰

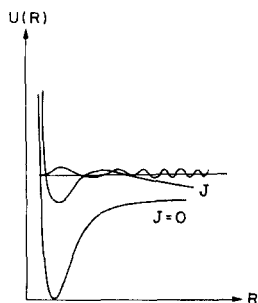


Fig. 4. Rotational predissociation in a diatomic molecule. The potential curve at finite values of the orbital angular momentum may support a metastable state, which escapes by tunneling through the hump in the potential.

The resulting expression for the decay rate is of the form

$$\frac{\Gamma_n}{\hbar} = \nu P \quad (4.2)$$

Here ν can be interpreted as the vibration frequency inside the well (i.e., the number of times per second that the system reaches the barrier), and P is the tunneling probability via the classically forbidden region.

An alternative approach is to solve the Schrödinger equation. If one does so, it is found that for most energies the wavefunction is very largely confined to the unbound region to the right of the barrier. At (and within a range of about Γ_n) certain energies the radial function has a large component within the well. These are the energies of the predissociating states. They can be approximated by the bound state energies in a problem where the barrier is made impenetrable (e.g., by making it much thicker). About such energies the density of states has a Lorentzian component

$$A_n(E) = \frac{\Gamma_n}{(E - E_n)^2 + (\Gamma_n/2)^2} \quad (4.3)$$

The delay time,²⁴ given by $\hbar A_n(E)$, is also maximal at E_n . These characteristics, that is, a large localized component of the radial wavefunction at an energy in the continuum, or equivalently an increase in the density of states/delay time, are usually referred to as a "resonance" or a quasibound state.

Such rotational predissociation is common in diatomics, providing the elementary dissociation channel on the ground-state potential curve. This process is expected to prevail for high-order multiphoton photofragmentation of diatomics, which can be accomplished only at extremely intense radiation fields,³⁹⁻⁴³ and which has not yet been experimentally documented. Evidence for rotational predissociation in polyatomic molecules is scarce, some evidence being reported for the occurrence of this process in HNO.²⁷ Of considerable interest is the inverse rotational predissociation (IRP) process involving a collision of the two constituents with angular momentum $\hbar J$ and energy $\sim E_n$, which results in the emission of an infrared photon to a lower bound state of the diatomic molecule. This process can be envisioned as the decay from a translational continuum via an intermediate state to a radiative continuum. Such IRP processes (e.g., the recombination of He + H⁺) are of considerable astrophysical interest.¹⁶¹ IRP of diatomics involves essentially a radiative recombination process. For IRP involving atom-diatom collisions, with the diatom being in a

vibrationally excited state, the decay channel can involve nonradiative vibrational predissociation. Rice⁷⁸ and Herschbach et al.⁷⁹ have recently suggested that the low-temperature vibrational relaxation of $I_2(B^3\Pi, v)$ by He occurs via IRP, with an orbiting resonance of $HeI_2(B^3\Pi, v)$ decaying into the dissociation channel $He + I_2(B^3\Pi, v-1)$.

All other predissociation processes on a given potential energy surface involve deexcitation of either rotational or vibrational degrees of freedom or both.¹⁶² Vibrational predissociation involves the decay of a metastable vibrational level of a polyatomic molecule into the dissociative continuum corresponding to the same electronic configuration (Fig. 5). This process was treated by Rosen's 1933 theory¹⁶³ of decomposition of metastable molecules. The appropriate classical description of vibrational predissociation involves the Lissajous motion of an image point on a multi-dimensional potential surface to the dissociative region. Unambiguous experimental evidence for vibrational predissociation in conventional polyatomic molecules was not well documented, as the dividing line between this intrastate process and the interstate electronic predissociation is vaguely defined.²⁷ From the theoretical point of view, a complete picture of vibrational predissociation of ordinary molecules requires the description of the nuclear level structure at highly excited vibrational states, and the elucidation of intramolecular intrastate vibrational energy flow in a strongly scrambled dense manifold, which in turn is coupled to a dissociation continuum.

Of considerable current interest are the intrastate predissociation processes that involve rotational or vibrational deexcitation of weakly bound complexes. Here the presence of an attractive well plays a key role. As the simplest example, consider a collision between an atom and a diatomic molecule at an energy not sufficient to, say, excite the vibration of the molecule. As the two approach, the attraction increases the available kinetic energy with the result that the diatomic can be excited, while the atom is now bound by the attractive force. The resulting species (see Fig. 6) is only quasibound, since it can predissociate by the process of transfer

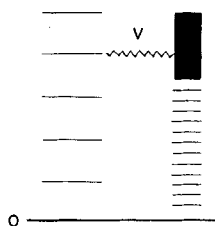


Fig. 5. Vibrational predissociation in a polyatomic molecule. Zero-order vibrational states located above the threshold of the dissociative continuum, corresponding to the same electronic configuration, are metastable, exhibiting an intrastate reactive relaxation process.

of the vibrational excitation of the diatomic back to the translation (V-T). Such quasibound states can also be formed by optical excitation from lower-lying states^{66, 67} and can dissociate by either V-T or R-T processes, or both of them. This mechanism is quite general, since even in the absence of chemical attraction the longer range van der Waals forces suffices to support bound states, and hence to give rise to such "subexcitation" quasibound states. In a predissociation, via an intramolecular V-T or R-T process, the energy required to promote the translation to a dissociative state is provided by the deexcitation of either the vibration or the rotation. Since even van der Waals wells are tens of wavenumbers or more deep, R-T predissociation requires a deexcitation of a rotational

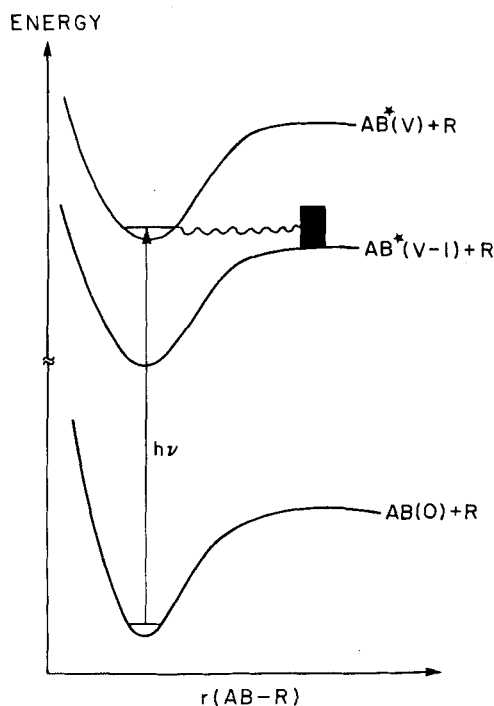


Fig. 6. Vibrational predissociation of the triatomic van der Waals molecule $AB-R$, where AB is a conventional diatomic molecule and R represents a rare-gas atom. Optical excitation from the ground electronic-vibrational state $AB(v=0)-R$ of the complex to the electronically-vibrationally excited state $AB^*(v)-R$ results in a quasibound state. This metastable state can decay via V-T into the translational continuum $AB^*(v')+R$, with $v' < v$, corresponding to lower vibrational states of the diatomic molecule. The VP process $AB^*(v)-R \rightarrow AB^*(v-1)+R$ is denoted by a horizontal wiggly line.

mode with a high B constant and would thus be typical of, for example, rare-gas-hydrogen-halides van der Waals bound pairs.¹⁶⁵

Recently, photofragmentation of the van der Waals molecules I_2R , ($R=He, Ne, Ar$) upon excitation of the I_2 molecule, has been demonstrated.^{66, 67, 164} Here the quasibound state is prepared by optical excitation to a vibrationally excited state of the $^3\Pi$ electronic state of I_2 and decays by a $V-T$ transfer. For the simple case of dissociation of $AB-R$ by direct intramolecular $V-T$ transfer (e.g., as is the case in I_2He), the rate of dissociation can be semiquantitatively described in terms of an exponential gap law¹⁴⁴

$$\Gamma = h\nu \exp \left[-\pi d \left(\frac{2\mu\epsilon}{\hbar} \right)^{1/2} \right] \quad (4.4)$$

Here [cf. (4.2)] ν is the effective frequency for the bound relative motion (of $AB-R$), and the second factor can be interpreted as the probability of the $V-T$ transfer. d is the range of the $AB-R$ interaction and μ is the reduced mass. ϵ denotes the released kinetic energy of the fragments, which is determined by the mismatch between the frequency of the AB vibration and the binding energy of the $AB-R$ mode. Such probability factors have indeed also been extensively discussed by $V-T$ transfer processes in $AB-R$ collisions.²

The exponential gap relation (4.4), which was derived¹⁴⁴ from the collision theory analysis is one member of a family of such relations. Equation 4.4 is isomorphous to the conventional Gamow formula (4.2) for tunneling of a particle of mass μ over a barrier of height ϵ and spatial extent d , providing a semiclassical description of intrastate overlap between bound and continuum nuclear states. The variation of the lifetimes of various triatomic $AB-R$ complexes, with respect to the $V-T$ vibrational predissociation process, exhibits a strong energy gap dependence and can vary over 20 orders of magnitude from the picosecond domain up to lifetimes comparable to the age of the universe.¹⁴⁴ This admittedly oversimplified description, which disregards rotational effects as well as the rate of the $R-AB$ vibrational bending mode, constitutes the essential conceptual framework for the understanding of vibrational predissociation in small model systems. Furthermore, these studies provide compelling evidence that the intramolecular vibrational energy flow in the $AB-R$ complex is not necessarily fast, in contrast to the intuitive arguments.

The energy-gap law addresses the dynamics of a direct vibrational predissociation process, where a single discrete state is coupled to a