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978-0-521-48414-5 - Photodissociation Dynamics: Spectroscopy and Fragmentation of Small Polyatomic Molecules

Reinhard Schinke

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Photodissociation induced by the absorption of single photons permits the detailed study of molecular dynamics such as the breaking of bonds, internal energy transfer and radiationless transitions. The availability, over the last decade, of powerful lasers operating over a wide frequency range has stimulated rapid development of new experimental techniques which make it possible to analyze photodissociation processes in unprecedented detail. At the same time, theorists have developed powerful methods to treat this fundamental process, at least for small molecules, in an essentially exact quantum mechanical way. The confluence of theory and experiment has greatly advanced understanding of molecular motion in excited electronic states.

This text elucidates the achievements in calculating photodissociation cross sections and fragment state distributions from first principles, starting from multi-dimensional potential energy surfaces and the Schrödinger equation of nuclear motion. Following an extended introduction in which the various types of observables are outlined, the next four chapters summarize the basic theoretical tools, namely the time-independent and the time-dependent quantum mechanical approaches as well as the classical picture of photodissociation. The discussions of absorption spectra, diffuse vibrational structures, the vibrational and rotational state distributions of the photofragments form the core of the book. More specific topics such as the dissociation of vibrationally excited molecules, emission during dissociation or nonadiabatic effects are discussed in the last third of the book.

It will be of interest to graduate students as well as senior scientists working in molecular physics, spectroscopy, molecular collisions and molecular kinetics.

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Photodissociation Dynamics

Spectroscopy and Fragmentation of Small Polyatomic Molecules

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Preface

Photodissociation of small polyatomic molecules is an ideal field for investigating molecular dynamics at a high level of precision. The last decade has seen an explosion of many new experimental methods which permit the study of bond fission on the basis of single quantum states. Experiments with three lasers — one to prepare the parent molecule in a particular vibrational-rotational state in the electronic ground state, one to excite the molecule into the continuum, and finally a third laser to probe the products — are quite usual today. *State-specific chemistry* finally has become reality. The understanding of such highly resolved measurements demands theoretical descriptions which go far beyond simple models.

Although the theory of photodissociation has not yet reached the level of sophistication of experiment, major advances have been made in recent years by many research groups. This concerns the calculation of accurate multi-dimensional potential energy surfaces for excited electronic states and the dynamical treatment of the nuclear motion on these surfaces. The exact quantum mechanical modelling of the dissociation of a triatomic molecule is nowadays practicable without severe technical problems. Moreover, simple but nevertheless realistic models have been developed and compared against exact calculations which are very useful for understanding the interrelation between the potential and the nuclear dynamics on one hand and the experimental observables on the other hand.

The aim of this book is to provide an overview of the theoretical methods for treating photodissociation processes in small polyatomic molecules and the achievements in merging *ab initio* calculations and detailed experiments. It is primarily written for graduate students starting research in molecular physics. However, experimentalists working in photochemistry, spectroscopy, unimolecular reactions, or molecular scattering, who are generally not very familiar with quantum mechanical methods for systems with more than one degree of freedom, also might

benefit from reading this monograph. The basic equations are confined to a simple level and derived in substantial detail. Rather than outlining the theory in full generality (which leads to vast amounts of indices which usually obscure the simplicity of the underlying molecular process) I concentrate on the discussion of the fundamental dynamical effects and their relation to the multi-dimensional potential energy surface. Elementary knowledge of quantum mechanics should be sufficient to follow the derivations.

Instead of reviewing the many systems which have been investigated experimentally up to now, I will highlight only a few examples in order to elucidate the main dynamical features. This includes H_2O , H_2O_2 , H_2S , ClNO , and CH_3ONO . For all these systems more or less complete potential energy surfaces have been calculated allowing rigorous dynamical studies without simplifying assumptions. Although experimental methods, which deserve a book for themselves, will not be explicitly discussed in this monograph, I will present many experimental results in order to illustrate the various aspects of photodissociation and the success of recent theoretical investigations. Despite the fact that this monograph covers mainly small polyatomic molecules, many of the general pictures may also apply to larger molecules. The photodissociation of diatomic molecules will not be considered explicitly except for illustration purposes.

The general theory for the absorption of light and its extension to photodissociation is outlined in Chapter 2. Chapters 3–5 summarize the basic theoretical tools, namely the time-independent and the time-dependent quantum mechanical theories as well as the classical trajectory picture of photodissociation. The two fundamental types of photofragmentation — direct and indirect photodissociation — will be elucidated in Chapters 6 and 7, and in Chapter 8 I will focus attention on some intermediate cases, which are neither truly direct nor indirect. Chapters 9–11 consider in detail the internal quantum state distributions of the fragment molecules which contain a wealth of information on the dissociation dynamics. Some related and more advanced topics such as the dissociation of van der Waals molecules, dissociation of vibrationally excited molecules, emission during dissociation, and nonadiabatic effects are discussed in Chapters 12–15. Finally, we consider briefly in Chapter 16 the most recent class of experiments, i.e., the photodissociation with laser pulses in the femtosecond range, which allows the study of the evolution of the molecular system in real time.

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Göttingen, 1992

Reinhard Schinke

Units: Throughout this monograph energies will be measured in eV or in cm^{-1} ($1 \text{ eV} = 8065 \text{ cm}^{-1}$ or $96.48 \text{ kJ mol}^{-1}$) and distances will be measured in Å or in a_0 ($1 \text{ Å} = 10^{-10} \text{ m}$; $1 a_0 = 0.52918 \cdot 10^{-10} \text{ m}$).

Abbreviations: Frequently used abbreviations are PES for potential energy surface and FC for Franck–Condon.