

Chemical Dynamics in Condensed Phases

*Relaxation, Transfer, and Reactions
in Condensed Molecular Systems*

Abraham Nitzan

OXFORD GRADUATE TEXTS

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Condensed Molecular Systems**

Abraham Nitzan

Tel Aviv University

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To Raya, for her love, patience and understanding

PREFACE

In the past half century we have seen an explosive growth in the study of chemical reaction dynamics, spurred by advances in both experimental and theoretical techniques. Chemical processes are now measured on timescales as long as many years and as short as several femtoseconds, and in environments ranging from high vacuum isolated encounters to condensed phases at elevated pressures. This large variety of conditions has led to the evolution of two branches of theoretical studies. On one hand, “bare” chemical reactions involving isolated molecular species are studied with regard to the effect of initial conditions and of molecular parameters associated with the relevant potential surface(s). On the other, the study of chemical reactions in high-pressure gases and in condensed phases is strongly associated with the issue of environmental effects. Here the bare chemical process is assumed to be well understood, and the focus is on the way it is modified by the interaction with the environment.

It is important to realize that not only does the solvent environment modify the equilibrium properties and the dynamics of the chemical process, it often changes the nature of the process and therefore the questions we ask about it. The principal object in a bimolecular gas phase reaction is the collision process between the molecules involved. In studying such processes we focus on the relation between the final states of the products and the initial states of the reactants, averaging over the latter when needed. Questions of interest include energy flow between different degrees of freedom, mode selectivity, and yields of different channels. Such questions could be asked also in condensed phase reactions, however, in most circumstances the associated observable cannot be directly monitored. Instead questions concerning the effect of solvent dynamics on the reaction process and the inter-relations between reaction dynamics and solvation, diffusion and heat transport become central.

As a particular example consider photodissociation of iodine $I_2 \leftrightarrow I + I$ that was studied by many authors in the past 70 years.¹ In the gas phase, following optical excitation at wavelength ~ 500 nm the I_2 molecule dissociates and this is the end of the story as far as we are concerned. In solutions the process is much more complex. The molecular absorption at ~ 500 nm is first bleached (evidence of depletion of ground state molecules) but recovers after 100–200 ps. Also some transient state

¹ For a review see A. L. Harris, J. K. Brown, and C. B. Harris, *Ann. Rev. Phys. Chem.* **39**, 341 (1988).

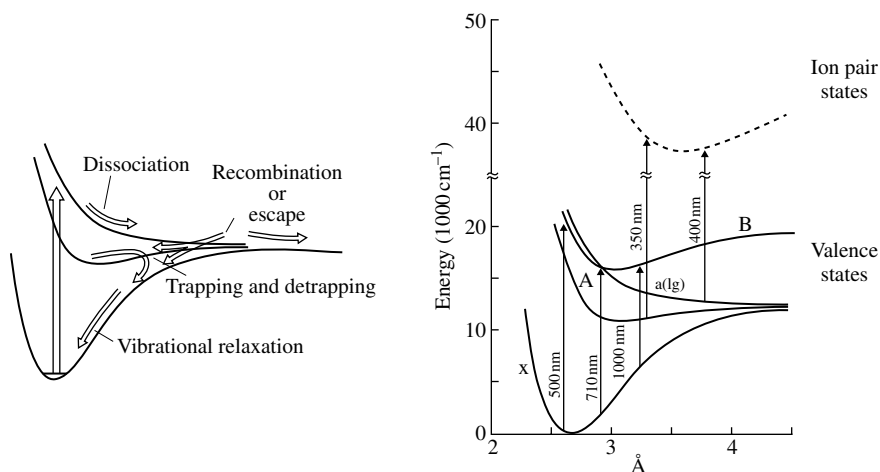


FIG. 0.1 A simplified energy level diagram for I_2 (right), with the processes discussed in the text (left). (Based on Harris et al. (see footnote 1).)

which absorbs at ~ 350 nm seems to be formed. Its lifetime strongly depends on the solvent (60 ps in alkane solvents, 2700 ps (=2.7 ns) in CCl_4). Transient IR absorption is also observed and can be assigned to two intermediate species. These observations can be interpreted in terms of the schematic potential energy diagram shown in Fig. 0.1 which depicts several electronic states: The ground state X, bound excited states A and B and a repulsive state that correlates with the ground state of the dissociated species. A highly excited state corresponding to the ionic configuration I^+I^- is also shown. Note that the energy of the latter will be very sensitive to the solvent polarity. Also note that these are just a few representative electronic states of the I_2 molecule. The ground state absorption, which peaks at 500 nm, corresponds to the $X \rightarrow B$ transition, which in the low-pressure gas phase leads to molecular dissociation after crossing to the repulsive state. In solution the dissociated pair finds itself in a solvent cage, with a finite probability to recombine. This recombination yields an iodine molecule in the excited A state or in the higher vibrational levels of the ground X states. These are the intermediates that give rise to the transient absorption signals.

Several solvent induced relaxation processes are involved in this process: Diffusion, trapping, geminate recombination, and vibrational relaxation. In addition, the $A \rightarrow X$ transition represents the important class of nonadiabatic reactions, here induced by the solute-solvent interaction. Furthermore, the interaction between the molecular species and the radiation field, used to initiate and to monitor the process, is modified by the solvent environment. Other important solvent induced processes: Diffusion controlled reactions, charge (electron, proton)

transfer, solvation dynamics, barrier crossing and more, play important roles in other condensed phase chemical dynamics phenomena.

In modeling such processes our general strategy is to include, to the largest extent possible, the influence of the environment in the dynamical description of the system, while avoiding, as much as possible, a specific description of the environment itself. On the most elementary level this strategy results in the appearance of phenomenological coefficients, for example dielectric constants, in the forces that enter the equations of motion. In other cases the equations of motions are modified more drastically, for example, replacing the fundamental Newton equations by the phenomenological diffusion law. On more microscopic levels we use tools such as coarse graining, projections, and stochastic equations of motion.

How much about the environment do we need to know? The answer to this question depends on the process under study and on the nature of the knowledge required about this process. A student can go through a full course of chemical kinetics without ever bringing out the solvent as a participant in the game—all that is needed is a set of rate coefficients (sometimes called “constants”). When we start asking questions about the origin of these coefficients and investigate their dependence on the nature of the solvent and on external parameters such as temperature and pressure, then some knowledge of the environment becomes essential.

Timescales are a principle issue in deciding this matter. In fact, the need for more microscopic theories arises from our ability to follow processes on shorter timescales. To see how time becomes of essence consider the example shown in Fig. 0.2 that depicts a dog trying to engage a hamburger. In order to do so it has to go across a barrier that is made of steps of the following property: When you stand on a step for more than 1 s the following step drops to the level on which you stand. The (hungry) dog moves at constant speed but if it runs too fast he will spend less than one second on each step and will have to work hard to climb the barrier. On the other hand, moving slowly enough it will find itself walking effortlessly through a plane.

In this example, the 1 second timescale represents the characteristic relaxation time of the environment—here the barrier. The dog experiences, when it moves

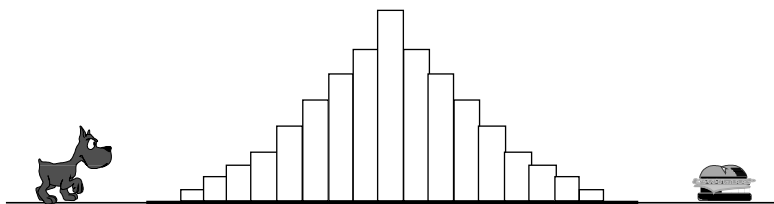


FIG. 0.2 The hamburger–dog dilemma as a lesson in the importance of timescales.

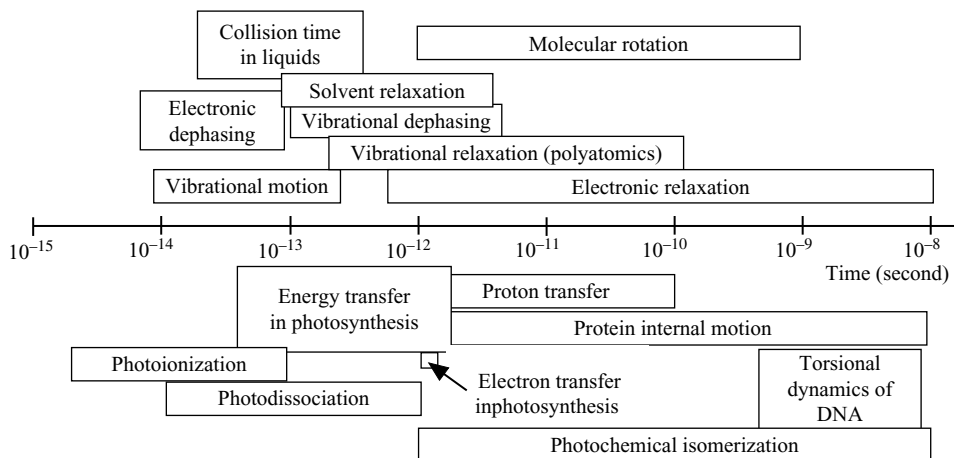


FIG. 0.3 Typical condensed phase molecular timescales in chemistry and biology. (Adapted from G. R. Fleming and P. G. Wolynes, *Physics Today*, p. 36, May 1990).

slowly or quickly relative to this timescale, very different interactions with this environment. A major theme in the study of molecular processes in condensed phases is to gauge the characteristic molecular times with characteristic times of the environment. Some important molecular processes and their characteristic times are shown in Fig. 0.3.

The study of chemical dynamics in condensed phases therefore requires the understanding of solids, liquids, high-pressure gases, and interfaces between them, as well as of radiation–matter interaction, relaxation and transport processes in these environments. Obviously such a broad range of subjects cannot be treated comprehensively in any single text. Instead, I have undertaken to present several selected prototype processes in depth, together with enough coverage of the necessary background to make this book self contained. The reader will be directed to other available texts for more thorough coverage of background subjects.

The subjects covered by this text fall into three categories. The first five chapters provide background material in quantum dynamics, radiation–matter interaction, solids and liquids. Many readers will already have this background, but it is my experience that many others will find at least part of it useful. Chapters 6–12 cover mainly methodologies although some applications are brought in as examples. In terms of methodologies this is an intermediate level text, covering needed subjects from nonequilibrium statistical mechanics in the classical and quantum regime as well as needed elements from the theory of stochastic processes, however, without going into advanced subjects such as path integrals, Liouville-space Green functions or Keldysh nonequilibrium Green functions.

The third part of this text focuses on several important dynamical processes in condensed phase molecular systems. These are vibrational relaxation (Chapter 13), Chemical reactions in the barrier controlled and diffusion controlled regimes (Chapter 14), solvation dynamics in dielectric environments (Chapter 15), electron transfer in bulk (Chapter 16), and interfacial (Chapter 17) systems and spectroscopy (Chapter 18). These subjects pertain to theoretical and experimental developments of the last half century; some such as single molecule spectroscopy and molecular conduction—of the last decade.

I have used this material in graduate teaching in several ways. Chapters 2 and 9 are parts of my core course in quantum dynamics. Chapters 6–12 constitute the bulk of my course on nonequilibrium statistical mechanics and its applications. Increasingly over the last 15 years I have been using selected parts of Chapters 6–12 with parts from Chapters 13 to 18 in the course “Chemical Dynamics in Condensed Phases” that I taught at Tel Aviv and Northwestern Universities.

A text of this nature is characterized not only by what it includes but also by what it does not, and many important phenomena belonging to this vast field were left out in order to make this book-project finite in length and time. Proton transfer, diffusion in restricted geometries and electromagnetic interactions involving molecules at interfaces are a few examples. The subject of numerical simulations, an important tool in the arsenal of methodologies, is not covered as an independent topic, however, a few specific applications are discussed in the different chapters of Part 3.

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