

Chapter 1

General Introduction

1.1 Chemical Dynamics in Liquid Solution

The majority of chemical reactions occur in the liquid phase. Knowledge of solvent dynamics is therefore of essential importance to the detailed understanding of chemical reactions in solution [1,2]. While for a photodissociation or isomerization reaction in the gas phase the excited state molecular potential is all determining [3,4], in the liquid phase collisions between reagent and solvent molecules also play an important role in the outcome of a reaction [5]. It was recently shown how the use of the interaction picture allows a formulation of solution dynamics in terms of "bare" observables corresponding to the gas phase species [6]. A much debated concept is the cage effect in liquid state chemistry [7], where the molecular fragments after photodissociation are held together by the neighbouring solvent molecules. Collision and friction between solvent and reactant molecules determine whether or not the fragments have a chance to recombine. For instance, time domain spectroscopy has been used to study the geminate recombination of iodine in solution since 1974 [8]. Recent results, however, lead to the conclusion that in this case more information has been obtained on vibrational relaxation than on the actual recombination process [1,9]. Nevertheless, the study of the cage effect is still a very active field and of prime importance to an understanding of collisional effects. The direct role of nuclear solvent degrees of freedom has also been indicated in electron- and proton-transfer reactions, both theoretically [10,11] and experimentally [12]. The study of the solvent dependence of isomerization reactions, like that of the excited isomers of stilbene, has attracted a lot of attention as well [2,13,14].

Currently much work is devoted to the modelling of chemical reactions in solution by molecular dynamics simulations [15] or by the use of the (generalized) Langevin [16-19] or Kramers [20,21] equations. A clear advantage of molecular dynamics studies is that the input is strictly microscopic in the form of intermolecular potentials. Unfortunately these potentials are not very reliable for many systems. Use of the Langevin or Kramers equations relies on the knowledge on the intramolecular potentials and bulk solvent properties such as viscosity and dielectric relaxation times. The

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common approach in both theories is that, out of the total number of degrees of freedom (reactant plus solvent), only the physically relevant ones (reaction coordinates) are dealt with explicitly. The others are accounted for in terms of a heat bath providing friction for motion along the reaction coordinate. In the case of the Kramers or Langevin theories it is also assumed that the frequency fluctuations of the solvent degrees of freedom occur much faster than the dynamics of the reaction. In the generalized Langevin equation (GLE) [18,19] such an assumption is not made leading to a frequency dependent friction kernel. So far however, little information is available concerning this kernel.

The characteristics of chemical reactions in liquids are determined by potential barriers as well as friction at the molecular level, where both of them are influenced by the reactant-solvent interactions. The shape of the potential barrier can be changed dramatically for a solvated reacting molecule with respect to the gas phase species, thereby speeding up or slowing down the reaction rate. The reactant is also influenced by the motions of the surrounding solvent molecules due to friction between reactant and solvent [2,22]. The reactant can exchange energy and momentum with the solvent. Friction can be due to both collisional as well as dielectric interactions. The collisions of solvent molecules onto the reactant hinder its motion, but also activate the reactant to cross the potential barrier. Dielectric friction is a consequence of the response of the solvent to a change in the charge distribution of the reactant molecules. This process is known as solvation dynamics [23].

1.2 Optical Dephasing and Solvation Dynamics

A first step in the goal of understanding liquid state dynamics will be the study of the influence of the solvent friction on the motions of a system without the additional effects of a chemical reaction. In this thesis the time evolution will be investigated of probe molecules in solution after optical excitation. The created electronic coherence of the probe molecules will exhibit phase relaxation due to interactions with the perturbing solvent molecules. These electronic dephasing processes in liquid solution turn out to be ultrafast: they occur on the femtosecond time scale [24,25]. The ultrafast electronic coherence decay corresponds to a large line broadening in frequency domain. A typical absorption spectrum of a dye molecule in solution at room temperature is shown in figure 1.1. One purpose of this thesis is to determine the time scale(s) of the solvent perturbations causing the ultrafast electronic dephasing in the liquid phase. Another purpose is to study the ultrafast characteristics of solvation dynamics, a

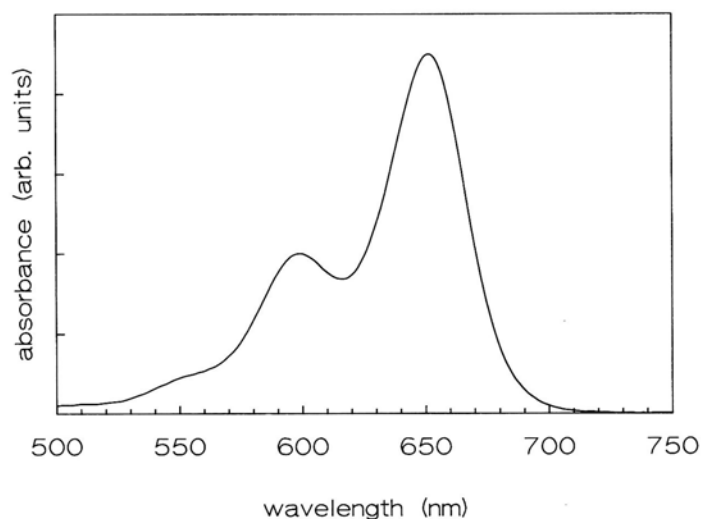


fig. 1.1 Absorption spectrum of the manifold of the first electronic transition of the dye molecule rhodamine 700 perchlorate in ethylene glycol at room temperature. The electronic dephasing processes typically induce a line broadening of hundreds of wavenumbers.

consequence of the response of the solvent to the change in the charge distributions of the probe molecules after optical excitation.

Three models will be used throughout this thesis that operate on different levels of sophistication. In fig. 1.2 the three models are schematically depicted. The electronic two level system, represented by the open circles, is coupled to the nuclear degrees of freedom of the solvent (represented by the boxes). Since the total number of nuclear degrees of freedom is very large for samples with macroscopic sizes, only some relevant ones will be considered explicitly (denoted by the open boxes in fig. 1.2). The influence of the remaining part of the nuclear degrees of freedom on the dynamics of the system will be averaged to constant parameters. This part will act as a heat bath, with which the system can exchange energy and momentum.

In the Bloch picture [26] the influence of the solvent on the probe molecule has been averaged to constant parameters. Here the time scale of the dynamics of the electronic two level system is much larger than the solvent's one. The electronic coherence will consequently exhibit a Markovian (exponential) decay.

In solution the optical dynamics of the probe molecules and the perturbations of the surrounding solvent occur on similar time scales. Henceforth the Markovian approximation for the system relaxation is not warranted. In this case more sophisticated models have to be applied for the description of experimental results than the conventional Bloch picture.

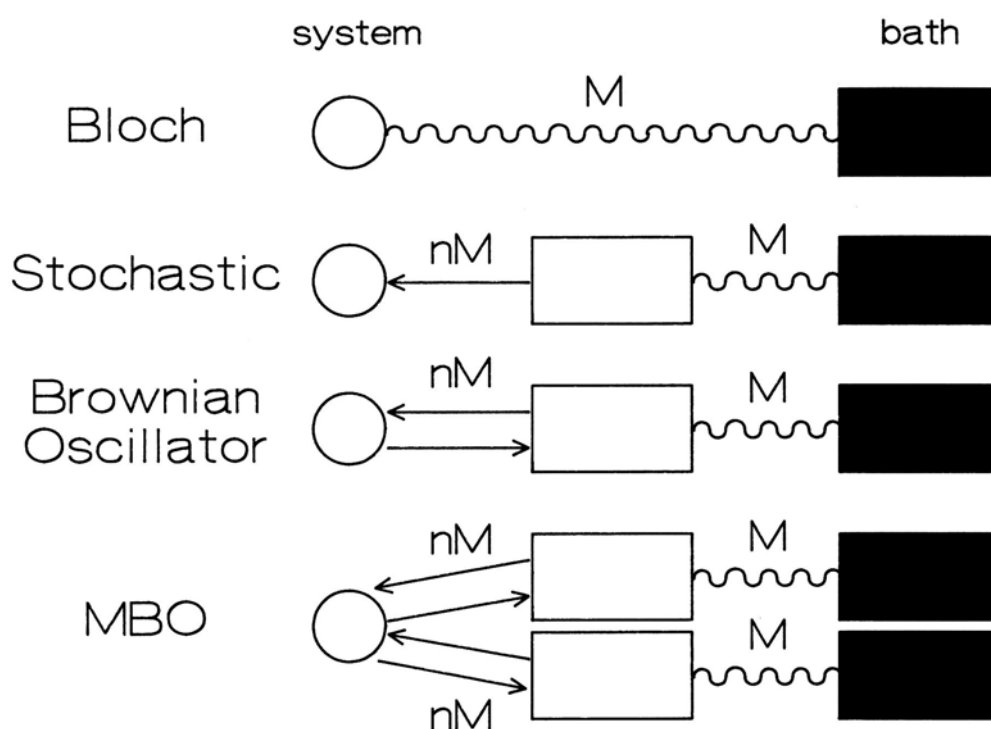


fig. 1.2 Schematic representation of the three models for optical dynamics that are used in this thesis. The system consists of two electronic levels coupled to nuclear degrees of freedom of the solvent (the bath). The rectangular unfilled boxes denote some specific solvent degrees of freedom that account for non-Markovian (nM) relaxation effects. These degrees of freedom are coupled in a Markovian (M) way to the remaining part of the solvent, represented by the filled boxes. For details see text.

In the stochastic model [27,28] the effect of the solvent motions lead to a stochastically modulated electronic transition. The electronic two level system has been "dressed" with a distribution of frequencies and a time scale of frequency modulation. In this case the system can exhibit a non-Markovian (non-exponential) decay, while the frequency modulation process acts in a Markovian way. The dynamics of the electronic system and the frequency modulation process can have arbitrary time scales.

In both the Bloch and the stochastic model the bath cannot respond to the evolution of the electronic system. This is a consequence of the assumption that the bath is so large that its motions are independent of the state of the system. In addition the temperature T of the bath must be so large that kT exceeds the excitation energy of the system (k is Boltzmann's constant). In contrast the multi-mode Brownian oscillator

(MBO) model [29,30] can account for a responding bath. A Brownian oscillator is an effective nuclear mode that is explicitly treated in the derivation of the time evolution of the system. This nuclear oscillator is coupled to the system in such a way that the latter can exhibit non-Markovian features. The dynamics of the nuclear oscillator is dependent on the state of the system. The oscillator is also coupled to the heat bath, making its motion identical to that of a Brownian particle. In the MBO model it is assumed that the dynamics of the heat bath are much faster than those of the Brownian oscillator. An advantage of the MBO model is the possibility of extension to a multitude of oscillators whenever appropriate.

In this thesis the results will be presented of a study on optical dephasing and solvation dynamics of the solute/solvent combinations depicted in fig. 1.3. The dynamics of optical transitions can be studied using a variety of spectroscopic techniques. In CW frequency domain techniques, like absorption and resonance light scattering spectroscopy, the response of the studied systems is obtained as a function of the frequency of one (or more) input (or output) steady-state optical fields. The influence of the fluctuations on the studied system are therefore sampled in frequency space. The shape of an absorption spectrum is determined by all fluctuations occurring on all time scales. Resonance light scattering spectroscopy is sensitive to fluctuations with time scales from femtoseconds up to the electronic lifetime (typically pico- to nanoseconds). Time domain spectroscopy on the other hand enables one to observe the dynamics in real time. Time domain four wave mixing techniques like two and three pulse photon echoes, but also chirped or incoherent two pulse scattering and pump-probe spectroscopy, are mainly determined by the ultrafast fluctuations with femto-second time scales. The intent is to determine the optical dynamics of a specific dye molecule in solution using as many spectroscopic techniques as possible, thereby separately probing the influence of fluctuations with different time scales. The interpretation of the results should give a consistent picture of the optical dynamics.

1.3 Outline of the Thesis

The contents of this thesis will briefly be outlined in this section. More extensive introductions will be given at the beginning of each chapter. Chapters 2 and 3 contain the theoretical background needed for the interpretation of the results. Chapter 4 treats the experimental details. Chapters 5 to 8 present the experimental results together with the interpretations. An attempt was made to present the work such that each chapter stands on its own. This has led to the repetitive character of the theoretical aspects in this thesis.

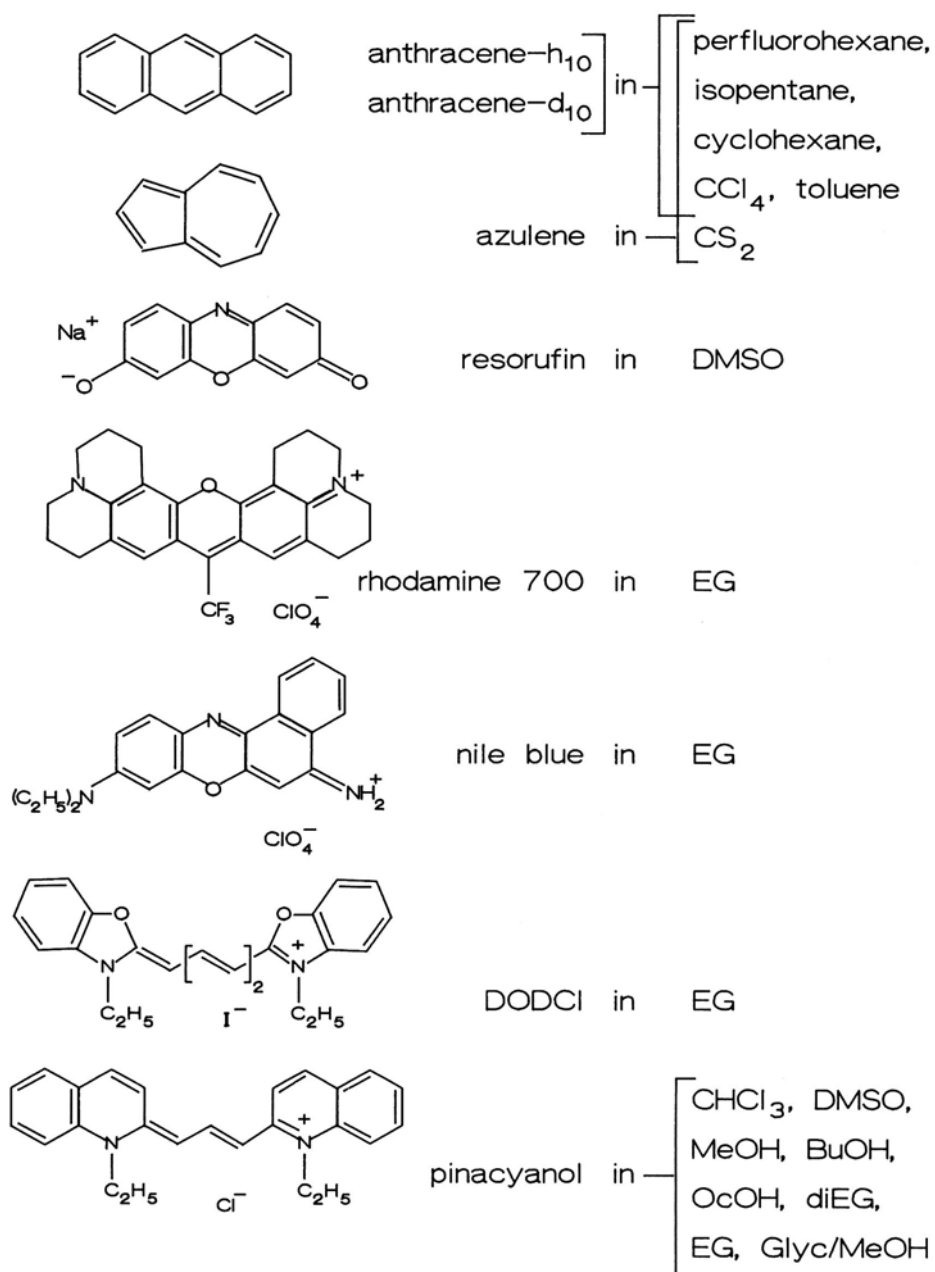


fig. 1.3 Summary of the solutions of which results are presented in this thesis. The dynamics of the first electronic transitions will be investigated, except for azulene of which also results on the second electronic transition will be presented. [DMSO = dimethylsulfoxide; MeOH = methanol; BuOH = 1-butanol; OcOH = 1-octanol; EG = ethylene glycol; diEG = diethylene glycol; Glyc = glycerol].

In chapter 2 the different theoretical models for the description of optical dynamics are treated. After the introduction of a model Hamiltonian for the optical systems the stochastic and multi-mode Brownian oscillator models are treated. A theoretical basis for these models is presented and specific expressions for the linear response function are evaluated. The chapter is concluded with a presentation of the hierarchy of sophistication in these models.

In chapter 3 a formalism for the description of different forms of (non-)linear spectroscopy will be introduced. This formalism is based on the assumption that the interactions between the studied systems and the applied electromagnetic fields occur in the perturbative limit. Expressions will be given for frequency domain linear absorption, relaxed fluorescence and resonance light scattering spectroscopy, as well as time domain four wave mixing techniques such as two and three pulse photon echoes, chirped two pulse scattering and pump-probe spectroscopy.

In chapter 4 the femtosecond experimental set-up will be described that was used for the performance of the time domain experiments. Especially the compression stage, where the femtosecond laser pulse duration time is shortened from 40 to 10 fs, will be treated in detail.

In chapter 5 a frequency domain investigation of the optical dynamics of anthracene and azulene in nonpolar solvents is presented. Absorption line shape analysis is used in the case of the first electronic transitions of anthracene-h₁₀ and anthracene-d₁₀, and the first and second electronic transitions of azulene. Resonance light scattering spectroscopy on the first electronic transition of azulene substantiates the line shape analysis results. The optical dynamics has a non-Markovian nature on a femtosecond time scale.

In chapter 6 the dynamics of the first electronic transition of resorufin in the aprotic polar solvent dimethylsulfoxide is investigated using the time domain two pulse photon echo and chirped two pulse scattering techniques. The absorption and emission spectra are also investigated. Using one Brownian oscillator all experimental results can be explained consistently.

In chapter 7 the technique of chirped four wave mixing is analysed more extensively. Using the example of the optical dynamics of resorufin in dimethylsulfoxide chirped two pulse scattering will be treated theoretically as well as numerically. Interesting features inherent to this technique make chirped pulse scattering a valuable new tool for spectroscopic problems.

Finally in chapter 8 some preliminary results of three pulse stimulated photon echo experiments on pinacyanol in various polar solvents will be presented. The experimental results show that pinacyanol has a more complex dynamical behaviour than resorufin.

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