

Chapter 1

Introduction

This thesis presents a contribution to ultrafast photodynamics of molecules in the condensed phase, which is a blooming branch of femtochemistry. The making and breaking of molecular bonds is the essence of chemistry, and these elementary steps occur on the ultrafast time scale of molecular vibrations (tens of femtoseconds, $1 \text{ fs} = 10^{-15} \text{ s}$). In 1999 Ahmed Zewail received the Nobel Prize in Chemistry for his fundamental contributions to the new field called femtochemistry, and its growth is documented in many recent proceedings [1–9]. The research in this field aims at an understanding of chemical reaction dynamics on a molecular level, in order to conceive new ways of controlling chemical processes [10–20], and this thesis is embedded in the special research project "Analysis and Control of ultrafast photoinduced reactions"¹. Various groups investigate increasingly complex systems, from isolated molecules in the gas phase (e.g. in molecular beams), over small molecules in liquids, up to large biomolecules in their native protein environment.

Research subject

The diatomic molecules ClF , Cl_2 and I_2 isolated in the solid rare gases Ar and Kr , which are investigated here, present conceptionally simple model systems. They show typical manybody or condensed phase properties such as dissipation, decoherence and nonadiabatic coupling; however, at a level of complexity which today can be handled theoretically. *Although the theory of the ultrafast dynamics of diatomic halogens in rare gases is well established, experimental data on the femtosecond timescale in these systems are scarce.* They are restricted to the large and heavy I_2 molecule in rare gases, and until now experimental pump-probe spectra with rather limited wavelength variation are analyzed via simulations [21–33]. In this thesis, the method of fs-pump-probe spectroscopy is used systematically to characterize the relevant ultrafast processes. It is especially well suited to study reactions of molecules in condensed phase environments, since conventional frequency domain spectra in the dissociation continuum are structureless and the solvent induces dynamical and structural broadening in the bound region, as well. The pump pulse triggers the dynamics, and the probe pulse records snapshots of the ultrafast processes at times set by the time delay between the two pulses. The laser induced fluorescence (LIF) is the recorded signal. The time resolution in such measurements is limited by the pulse duration. Pump and probe pulses use spectroscopic characteristics of the molecules to select reactants, products and electronic states; the LIF is an additional fingerprint of the molecules. Recent progress in the generation of tunable fs-laser-pulses promotes spectroscopically adapted fs-pump-probe experiments [34, 35]. Two improved non-collinear optical parametric amplifiers (NOPAs) are constructed to provide fs-pulses in a wide wavelength range and the short pulse duration is optimized in situ with a versatile implementation of the frequency-resolved optical gating (FROG) technique.

The goal of this thesis is to generate systematic sets of experimental data, which allow an extraction of the relevant information without the aid of simulations in order to provide an independent

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check that may validate the theoretical formalism and calibrate simulation parameters. The experimental study includes the two limiting cases of the large and heavy halogen I_2 in Kr and the small and light interhalogen ClF in Ar and Kr . Some results on the intermediate Cl_2 are also presented. The electronic structure of halogens and interhalogens is very similar. The basic differences determining the dynamics are the size and mass of the constituents. The I_2 molecule is fixed in the axial geometry of the double substitutional site. ClF is embedded in a nearly spherical cage. The reactive F fragment can move around the Cl atom within the matrix cage or even leave the first solvent shell to be trapped as a radical or to form a new molecule.

Since the research project aims at photochemical reactions, the focus of the investigations lies on strong interactions of the molecules with their solvent environment, which cannot be regarded simply as a perturbation of an isolated molecule. Therefore, the experiments involve excitation close to or above the gas phase dissociation limit. A wide range of phenomena typical for condensed phase photodynamics is extracted directly from the spectra and compared to detailed molecular dynamics simulations from the literature and cooperation partners. The results of the pump-probe experiments are presented in chapter 6. The discussion in chapter 7 comprises the following ultrafast processes:

- the dynamic cage effect (ch. 7.1)
- energy dissipation with a detailed account of the fragment-cage dynamics (ch. 7.3)
- maintenance of vibrational coherence despite strong dissipation (ch. 7.9)
- ultrafast reorientation of the molecular bond (ch. 7.5)
- non-adiabatic transitions including ultrafast solvent-induced spin-flip (ch. 7.6) and
- ultrafast dissociation versus recombination of the fragments (ch. 7.7). Finally,
- control of the yield of Cl^+Cl^- vs. Cl^+F^- formation is demonstrated (ch. 7.8).

Before the ultrafast photodynamics of the ClF molecule are analyzed, important properties of the molecule ClF have to be investigated. The experimental results are presented in chapter 4 and discussed in chapter 5 with respect to

- spectroscopy of ClF in Ar and Kr (ch. 5.1 and 5.2) and
- photodissociation yield of ClF in Ar and Kr (ch. 5.4).

As an introduction to the system diatomics in solid rare gases, chapter 2.1 summarizes the early work on classical molecular dynamics simulations of I_2/Kr and F_2/Ar , which provides an intuitive picture of the microscopic dynamics. Although the classical trajectories already show many of the dynamical processes of interest, a semiclassical extension that allows the description of nonadiabatic transitions between electronic states is inevitable. A basic description of wave packets is introduced as well. The concept pursued in this thesis is to extract information directly from the measured spectra without the aid of simulations. A theoretical background on typical phenomena in the condensed phase (matrix) is prepared in chapter 2.2 in order to provide heuristic arguments for the discussion of the condensed phase spectroscopy and dynamics. It includes the cage effect, cage exit and nuclear rearrangements, as well as excimers, ionic states and polarization effects. Chapter 2.3 discusses the method of fs-pump-probe spectroscopy with laser induced fluorescence (LIF) detection, with an emphasis on the specialties that occur in the condensed phase. It is the main experimental method employed in the thesis (part II). Chapter 2.4 provides the literature on the ClF molecule, since this thesis presents the first account of excited electronic states of ClF in condensed media and for the first time fs-spectroscopy is applied to ClF .

The experimental setup is described in chapter 3. Besides the preparation of the corrosive gas ClF in solid rare gas samples, the generation and characterization of tunable ultraviolet femtosecond pulses was implemented. The pulses are generated by frequency doubling the visible output of a non-collinear optical parametric amplifier (NOPA), and one of the major technical advances in this thesis was to double the efficiency of the NOPAs (chapter 3.4). A versatile variant of the frequency-

resolved optical gating (FROG) technique was developed to measure the UV pulses in situ, i.e. on the substrate, together with the pump-probe scan.

Motivation of the model system

Several groups advance theories that allow a description of molecular dynamics and reactions in inert rare gases (*Rg*) as a model solvent [36–38]. In experiments and theory, this conceptionally simple modular construction set, consisting of *Rg* solvent atoms and various solute molecules, allows isolation of the species of interest and the investigation of the molecule-solvent interaction. Structural properties of the model solvent can be varied from gas [39,40], over clusters [41] and liquids [42–44], to solids [41,45,46]. Parameters like the polarizability and lattice constants change from *Ne* to *Xe*. The investigation of cold and ordered samples, i.e. the solid rare gas matrices examined in this thesis, simplifies the theoretical description, since thermal averaging is reduced and the initial geometry is well defined. Historically, the study of halogen-rare-gas excimers and exciplexes in theory [47–51] and experiment [52–57] has focused considerable attention on diatomic halogens in *Rg*, resulting in precise potential energy surfaces. Both classical and detailed non-adiabatic molecular dynamics simulations of I_2 [58–66] and F_2 [67–73] in *Rg* were recently published.

On the experimental side, matrix isolation spectroscopy of various molecules and even highly reactive radicals in solid rare gas matrices has generated a large pool of spectroscopic knowledge of isolated species [74–78], and a recent review [36] summarizes the aspects of particular importance to this thesis. The spectroscopy of I_2 [79,80] and F_2 [81–84] in *Rg* is well established; however, molecular states of F_2 lie unfavorably far in the ultraviolet. Considering the photodynamics, I and F represent two extrema. Static experiments on photodissociation prove that for I_2 , the cage effect is complete and all fragments geminately recombine [85], whereas F atoms show high cage exit probability [53,86,87] and mobility [88] in *Rg* matrices. Even the penetration depth in layered rare gas samples was measured [89,90]. In this thesis, the interhalogen ClF was preferred to the halogen F_2 for spectroscopic reasons, although the spectroscopy had to be established first (chapter 4). All other F containing interhalogens are unstable against disproportionation to XY_3 and therefore more difficult to handle [91]. ClF is expected to display a wide range of interesting dynamics, and it offers the perspective to finally control a photochemical reaction in the condensed phase model-environment of solid rare gases. The F fragments not only form excimers and exciplexes like KrF and Kr_2F with the matrix atoms, but also triatomic molecules like $ClXeF$, $FXeF$ and $FKrF$, which are bound in the ground state [92–95]. The first *Ar* containing molecule, $HArF$, was found only two years ago [96] and the new rare gas containing molecule $ClKrF$ is predicted to be stable [97].

The theoretical description of ultrafast processes in the condensed phase is also a subject of active research, and dihalogens in rare gas matrix provide tractable model systems. According to the Fourier transformation, the ultrafast timescale is connected to broad spectra [98], which results in the excitation of wave packets synthesized from a coherent superposition of states [99,100]. The full quantum mechanical description can only be carried through for small systems with a few degrees of freedom. Large molecules and condensed phase systems have many degrees of freedom. Reduced dimensionality approaches and a wealth of semi-classical methods are investigated to tackle the challenges [99]. Semi-classical descriptions receive their justification from the spatial localization of the wave packets that persists on the femtosecond timescale. The motion of classical particles is approximated by wave packets, as stated in Ehrenfest’s correspondence principle [101]. In order to break a molecular bond, enough energy must be localized in this region. The coupling to other degrees of freedom leads to rapid dissipation of energy in the condensed phase or equivalently to Intramolecular Vibrational Redistribution (IVR) in larger molecules, counteracting this localization of energy [6]. Semi-classical theories describe the motion and interaction of the nuclei in great detail, and refinements for the quantum effects of delocalization, tunneling and interference can be made [102,103].

The presence of the solvent fluctuations that randomly change the dynamics of the solute molecule destroys the quantum coherences, and it is an open question how coherence in the condensed phase is accessible to external control. Another important complication originates from the coupling of different electronic states, which must be incorporated into theories, since most chemical reactions involve excited electronic states. These non-adiabatic effects receive increasing attention as computer power allows the treatment of the interplay of electronic and nuclear motion in complex systems [99]. To test the predictions of these advanced theoretical treatments, it is necessary to derive the relevant information from systematic experiments as it will be shown here. The close collaborations with the theory groups of Prof. J. Manz and Prof. R.B. Gerber within the Sfb450 is mutually stimulating for experiment and theory of the model system diatomics in condensed rare gases.