Chapter 1

Introduction

1.1 Overview

Condensed phase reaction dynamics presents a field of rapidly growing interest. It is feasible to gain insight into features of fundamental chemical relevance like on the femtosecond timescale the making and breaking of bonds, or the interaction with the environment. Since the development of the matrix-isolation technique in the 1950's by Pimentel et al. ([17, 18]) and the investigation of laser techniques on the femtosecond timescale, informations concerning the dynamics of these systems can be acchieved. By comparing these experimental results with that of the free molecules in the gas phase, a lot can be learned about the influence of the environment on the physical properties of the guest molecule and the nature of the interactions between the guest and the host atoms.

One model to study the photodissociation dynamics of molecules and by this the influence of the environment is to embed the molecule in a rare gas matrix, which has been performed by several groups with focus on a variety of topics [20, 23, 75, 33, 34, 78, 39, 37, 46]. Among these are for example predissociation or dissociation, recombination and trapping, vibrational relaxation and energy dissipation in the lattice, lattice dynamics and the mobility of atoms in a condensed medium. For resolving the complexity of the ongoing processes, the interpretation of experimental data has to be supported by theoretical calculations.

The choice of rare gases as environment provides several advantages: the crystal structures are simple, face centered cubic, the pair potentials between them are well defined and can be reproduced by Lennard-Jones or Morse functions. In addition, the inert nature of the rare gases reduces the probability for chemical

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reactions with the environment, even though new simulations performed by the group of R.B. Gerber predicted the formation of an organic krypton compound formed after photodissociation of acetylene in a krypton matrix, which could be confirmed experimentally [35, 36].

In principle, one can focus on the dynamics of the embedded molecule, to which will be referred to as the chromophore, the influence of the environment and, connected to this, phenomena which will arise from interaction of the molecule with the environment and the energy dissipation in the lattice.

On a ultrashort timescale, the photodissociation dynamics of the chromophore in condensed phases resembles the dynamics of the gas phase. Fig. 1.1 shows the most important possible processes from the view of the molecule.



Figure 1.1: Overview: Processes in condensed phase dynamics.

First the molecule will be promoted to an electronically and vibrationally excited state. Due to the repulsive potential, it will start to dissociate. These processes will take place on the femtosecond timescale, where the influence of the environment can be regarded as very small and thus they are similar to the processes in the gas phase.

The next possible steps are characterized by state transitions and will occur in regions, where the separation between the potential energy curves decreases, due to either avoided crossings as a property of the molecular potentials, or by interaction with the solvent. The dashed line in Fig. 1.1 shows the bending of the potential caused by the surrounding atoms. This effect, the so called *caging* will be discussed in the next section, 1.2. Depending on the energy of the embedded molecule and its orientation relative to the solvent atoms several pathways exist:

• *predissociation*: in the case of nonadiabatic crossings, predissociation can occur. This means just population transfer from a bound to a dissociative state by nonadiabatic transition and represents the first possibility for state transitions, see Fig. 1.2. In the adiabatic picture, this will be represented by avoided crossings, see dashed lines in Fig. 1.2



internuclear distance

Figure 1.2: Predissociation. The circle depicts the region where in the diabatic representation the states cross and state transitions due to intersystem crossing are possible. The dashed lines in this area depict the adiabatic representation, which shows an avoided crossing.

- *dissociation*: if the energy of the molecule is higher than the potential barrier due to the surrounding atoms, the molecule will be able to dissociate. This means at least one of the fragments will leave its initial cavity and the corresponding bond will be broken. See Fig. 1.1, cage exit. See also section 1.2.
- *recombination*: State transitions may be induced by, for instance, the bending of the potential, due to the interaction with the solvent atoms, see the dashed line in Fig. 1.1. Subsequently, the molecule will be found in a vibrationally excited state. If the transition will lead to the ground state, after vibrational relaxation the bond will be rebuild. This relaxation includes probably more collisions with the matrix atoms or thermalization.
- *trapping*: if the transition will lead to another bound excited state, the molecule is trapped. It can relax vibrationally to its potential minimum or, if it has enough energy, start to oscillate. In this case, when it reaches its outer turning point, again state transitions, for example to the ground state, will be possible. Again it will lead on a higher vibrational state and vibrational relaxation will occur.

Usually combinations of these processes will occur. One sequence could be first photoexcitation of the chromophore, followed by vibrational relaxation, predissociation and recombination. All of the processes happening after the first encounter with the solvent molecules will also start some lattice dynamics and the dynamics of the molecule will not be decoupled from the surrounding atoms anymore. Because of the complexity of the systems and interactions, the influence of the environment will be introduced first before discussing the general phenomena of solid state dynamics like vibrational relaxation, dissipation and dephasing.

1.2 Cage Effect

Molecules soluted in liquids or embedded in a matrix will change their behaviour due to the effect of the surrounding atoms, either by the potential arising from the host atoms or from direct collisions. These interactions are called *Franck-Rabinowitch-* or *cage* effect. They can be observed in systems starting from small clusters to extended crystallographic structures, like small molecules embedded in rare gas matrices.



Figure 1.3: Definition of orientation in the cage: a) guest molecule pointing to cage windows, e.g. F_2 b) guest molecule pointing to cage wall, e.g. Cl_2

First, let us give a definition for the cage: It consists of the surrounding rare gas atoms in the vicinity of the *guest*, which could be a molecule or atom, and will be characteristic for the site and orientation of the chromophore in the *host* lattice structure. From the energetic point of view the guest will perceive infinite potential barriers at the locations of the host atoms, but in the spacing between them the barrier will become finite. Following Schwentner and Apkarian in their review of molecular photodynamics in rare gas solids [19], two distinctions are made for these areas: the *cage wall*, where the kinetic energy of the fragments is lower than the (infinite) barrier and the *cage windows*, where the kinetic energy may be higher than the barrier and cage exit is possible. Fig. 1.3 shows two possible orientations of a diatomic molecule in a face centered cubic lattice buildt of rare gas atoms. Different dynamics can be expected for the two different orientations and principally it can be distinguished between four different mechanisms of caging as shown in Fig. 1.4.

Panel a) shows *sudden exit*, which is possible for very light and/or small fragments like H or F atoms in lattices of comparatively large atoms, where excitation of the chromophore will provide the fragments with a kinetic energy higher than the barrier. In this case the fragments will be able to move through the environment, until repelled or deflected by cage walls in neighbouring cages. Sudden exit is only possible if the initial orientation of the chromophore points to a cage window. Sudden exit can lead to dissociation, but also recombination

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Figure 1.4: Mechanisms for caging: a) sudden exit, b) delayed exit, c) forced exit, d) perfect caging , adapted from [19]

can be observed. *Delayed exit* is shown in panel b), in which the molecule usually is oriented in the direction of a cage window, which could be opened by energy transfer to the respective window atoms so that the barrier (dottet line) will be lowered sufficiently enough for cage exit. One possible orientation, where delayed exit is preferred is shown in Fig. 1.3, panel a). Since delayed exit requires a movement of the closest packed lattice atoms, it can also be observed preferably for small guest molecules. In c) three snap-shots taken with evolving

time are depictet. This kind of *forced exit* requires, implemented by the name, a fragment with sufficiently high kinetic energy that forces its way out of the cage followed by rearrangement of the cage atoms and thus resulting in cage exit. Finally d) shows *perfect caging*, the most common case in previous studies. As an example compare Fig. 1.3, panel b). The diatomic in the rare gas lattice points directly to a cage wall, or an rare gas atom respectively. Here the barrier is too high to be overcome by the molecular fragments and, also depending on the orientation of the molecule in the cage, the kinetic energy could be transferred to the lattice and dissipates away from the impurity, so that delayed exit is not possible anymore. Perfect caging works for large atoms or molecules with equal or sufficiently higher mass than the host atoms.

Which of these effects will occur depends both on size and mass of the guest molecule and the fragments, respectively, and the chromophore's initial orientation in the lattice. It has to be emphasized at this point, that in the regions, where the potential energy curves, compared to the gas phase potentials, bent up due to interaction with the matrix atoms, the energy differences between the states will become very small. In this area some of the states will be nearly degenerated and the mixing of the formerly pure states will not be negligible anymore. Now state transitions become an important channel for the following dynamics.

1.3 Chromophore Dynamics

Phenomena like state transitions, vibrational relaxation and dephasing of the initial wavepacket are similar to the same processes in the gas phase, but will change their characteristics significantly in an environment. For example, state transitions will be much enhanced and vibrational relaxation will occur not only radiatively like in the gas phase, but mostly because of collisions with the environment atoms. In addition some of the phenomena described here, like energy exchange with the environment and the so called matrix shift will be characteristic for condensed phase dynamics.

Coming from the gas phase, also the potentials of the chromophore will change, see for example the matrix shift. In general, we will get a mixing of the pure states of the gas phase, resulting in Born-Oppenheimer adiabatic states. At internuclear distances where the influence of the matrix is assumed to be small, these adiabatic

states can be classified by their main character regarding the 'pure' states. Then after excitation of the guest molecule, state transitions can occur, for instance, population transfer from a singlet to a triplet state.

matrix shift : insertion of a small molecule in an environment leads to some general changes in the potential energy of the molecular states. The total energy of the state compared to the gas phase potential will be modified, for example usually a small redshift will appear for molecules embedded in argon or a blue shift for molecules embedded in neon matrices [52]. Second, there will be a relative shift of the vibrational frequencies, but except for some halides the deviations will only be around 2 % from the values of the gas phase. Both phenomena were studied systematically by Jacox et al [52]. For ionic or Rydberg states the shift will be much larger, due to the polarizable environment and larger spatial distribution of the outer orbitals in case of Rydberg states, which will interact with the solvent atoms. [53]

energy exchange : another effect, which has to mentioned in this context, is the energy exchange with the solvent. During the dynamics of an excited molecule in an environment, one has to be aware that the potential energy of the chromophore will change because of shiftings of the cage atoms, see for example in Fig. 1.5 the lowering of the potential due to collision events with the medium. After photoexcitation the chromophore will start to dissociate, until it encounters the cage atoms. Depending on the initial site and orientation, shiftings of the lattice atoms can be initialized, without direct collisions. In panel d) of Fig. 1.4, the mechanism for perfect caging, the atom will not only interact with the atoms in direction of its momentum, but also with other atoms perpendicular to it. The oscillations of lattice atoms, initialized by the movement of the chromophore after photoexcitation, can also lead to a case, where energy is transferred *back* to the chromophore in the course of the dynamics. Again this will add to the complexity of pump-probe spectra and will be discussed in the corresponding section 1.5.

state transitions : as discussed in section 1.1, state transitions can occur in regions, where the potential energy curves converge. Here due to the influence of the environment the adiabatic states will change their initial character, which can

be shown by projection on the pure states of the molecule. One possible state transition, predissociation, was already mentioned in section 1.1. In condensed phase dynamics the potential energy surfaces may converge also when the molecular fragments approach the cage. The bending of the potential, shown schematically as a dashed line in Fig. 1.1 will merge the adiabatic states. This convergence of the states leads again to a mixing of the pure states, since the spin-orbit coupling (as a molecular property) or the perturbation of the states due to the cage atoms may exceed the energetic gap between the states.

Experimentally, for example, for the system ClF in Argon such kind of state transitions were observed, by changing the character from a singlet Π to a triplet Π state, thus indicating a (forbidden) spin-flip. 50 % of the population of the initially excited ¹ Π -state can be found in the lower lying ³ Π state after the first bond stretching of the molecule [16].

vibrational relaxation : in contrast to predissociation, vibrational relaxation of molecules embedded in an environment can be not only radiationally like in the gas phase, but instead will be supported by inelastic collisions with the host atoms. Therefore this process will be accelerated and thus becomes competing or cooperating to predissociation.

Fig. 1.5 shows the mechanism of vibrational relaxation. When the molecule reaches its outer turning point, it encounters the cage atoms and will interact with them. Energy will be transferred to the lattice, depending on the initial orientation of the chromophore in the surrounding and on the mass ratio between guest and host. For an effective energy transfer, the masses should be similar, so that the transfer of momentum will be nearly complete. As mentioned in section 1.2, in the case of delayed exit the first collision of a fragment with the window will start opening it and therefore lowers the potential, depicted by the dashed line in Fig. 1.5. In the case of perfect caging, the encounter with lattice atoms will not open any window, but during the collision kinetic energy will be transferred to the cage atom and will be further dissipated in the lattice, see section 1.4. Recombination of the chromophore to a lower vibrational state can occur if the molecule is able to transfer sufficient energy to the environment.

decoherence/dissipation of the wavepacket : the spreading of an initially focussed wavepacket is called dissipation and can be observed for any anharmonic potential. Usually several vibrational levels of the will be excited when the



Figure 1.5: Vibrational relaxation: after excitation the molecule starts to dissociate, until it hits the potential barrier due to the caging atoms. There it looses some energy and returns to the inner turning point, where again some amount of energy is lost, until it finally relaxes after several oscillations to the ground vibrational level of the excited state. The dashed line on the right depicts the lowering of the potential due to the guest-host interaction, resulting from rearrangements of the caging atoms.

molecule is promoted to a higher electronic state and additionally to the dissipation of the wave packet, the scattering events with the cage will lead to further decoherence. In the collision event, the phase relation between the former coherent superpositions of the wavepacket is destroyed. While this effect is neglected in the classical simulations performed in this work, it will add to the complexity of the experimental pump-probe spectra and, further discussion see section 1.5.

formation of new molecules : the last effect will be the formation of new molecules, which will be stabilized due to the environment. Gerber et al, who investigated theoretically the dynamics of several small molecules in rare gas matrices, like HCl, F_2 or acetylene, found evidence that after photodissociation of the chromophore and subsequent sudden or delayed cage exit of at least one of

the fragments, new molecules will be build, including the chromophore and one of the rare gas atoms. They proposed for example the first neutral organic krypton compound, HKrCCH, from the photodissociation of acetylene in a krypton matrix, which was confirmed by experiments [36].

1.4 Lattice Dynamics

As mentioned in the previous sections, guest and host dynamics will influence each other. This section will focus on processes related to energy transfer and relaxation mechanisms initiated in the solvent. On one side there will be direct energy transfer by collisions, as mentioned in the previous section in connection with vibrational relaxation. On the other side oscillations of the lattice atoms can be induced by the excitation of the chromophore and the following dynamics *without* direct transfer of momentum. While the first process can be understood in the sense of energy transport through the solvent and should dissipate very fast, the second process may induce oscillations or phonon modes on a much longer time scale. Both effects result, however, from the nonequilibrium excitation of the lattice due to photoexcitation of the guest molecule.

1.4.1 Shock Waves

Most of the vast literature and data bases dealing with shock waves are associated with explosives technology and shock-induced chemistry or material science [83, 84, 85, 86]. Investigation of energy transport and transfer, respectively, will be important for surface science, since the processes are related to those of sputtering experiments, where particles or molecules can be desorbed from surfaces [44].

In systems like dihalogens in rare gas matrices, the phenomenon of shock waves is connected to the cage effect, photoexcitation and subsequently recombination and vibrational relaxation. Sputtering events are described by energy transport phenomena from the bulk of the crystal to the surface. Energy transfer by collisional sequences presents a favourable channel for energy release in the solvent. In contrast to heat conduction, this process is highly anisotropic. Shock waves may occur in systems showing delayed or perfect caging, with high

efficiency in the latter case. In this case the photoexcited fragments will be in-

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volved in direct collisions, providing a efficient energy transfer to the lattice. This scheme can be seen in Fig. 1.6. At this time, energy in form of momentum will be transferred to the environment, the efficiency depending on the orientiation and the mass ratio of guest and host atoms [44]. The following collisions of lattice atoms will then transport the energy through the lattice, giving a sequence of binary collisions along this axis. This is often called a 'focussed' collision sequence. The energy transported in this way is primary kinetic energy, transported in the direction of close packed {110} chains and only a smaller fraction of the energy dissipates off this main axis [37, 44]



Figure 1.6: Scheme for shock wave generation: after the initial pulse the molecule starts to dissociate, until stopped by the next lattice atom. The momentum is transferred through a chain of atoms, constituting the shock wave.

Gabriel et al give a characterization of shock waves as follows:

"... a shock wave is classified by sharp discontinuities for energy, density, pressure, etc., arising at a wave front, which propagates through the medium" [37].

Here the energy transfer and relaxation mechanisms of solid argon after excitation of a single particle was investigated, thus generating an energy spike in the system. The energy is transported through the medium in a set of (elastic) collisions as described above, preferring the closest packed $\{110\}$ direction of the crystal, while the energy transfer in the transversal directions is much weaker. The front of the shock wave is sharp with no significant broadening of the kinetic energy, resulting in rather sharp peaks, while the reduction of the kinetic energy in time assigned to the particle at the front indicates energy dissipation in the lattice. The shock wave usually moves with supersonic velocity. The energy transfer from the first excited particle to the lattice will be on a timescale of approximately 100 fs and the energy in the lattice will relax into thermal distribution after 100 ns. The efficiency of the energy transport is very high, due to the equal masses of the atoms involved. Again, comparing to sputtering investigations, it may be interesting to remark, that the generation of a pulse with 1 eV excess energy at 20-30 Å apart from the surface of a crystal (in this simulation the crystal consisted of 2916 Ar atoms, thus meaning 9 unit cells in each direction) will still have enough energy to overcome the binding energy on the surface and thus will be ejected. This fact may play an important role in the choice of the model system and the use of periodic boundary conditions, but this will be discussed later.



Figure 1.7: Shock waves, taken from [43]. Panel a) shock wave calculated for equal masses of guest and host molecules in $\{110\}$ direction, panel b) energy distribution transversal to the $\{110\}$ direction, forming a wake

Another simulation was performed by Martens et al [43] for the energy distribution in a two-dimensional lattice, using the system I₂ in 2498 Ar atoms. This time the energy spike is generated by photoexcitation of the embedded halogen molecule. Again the main channel for energy transfer is a shock wave in the favoured {110} direction. Initially the molecule is oriented on this axis, showing perfect caging. Simultaneously to the favored direction a *wake* appears, see Fig. 1.7, showing that some part of the energy is transported off the main axis. Due to the mass ratio of I/Ar =3.18, the transfer of momentum in the first

collision with the lattice atoms is not perfect, so the iodine fragments are left with a sufficient amount of kinetic energy to produce a second wave. Shock wave simultations were performed for different mass ratios of guest and host molecules and the result of similar masses are shown in Fig. 1.7 on the left panel. Again the dissipation of energy along the main axis is dominant and the shock wave will overcome distances of more than 70 Å, while energy transfer to off axis regions is much more short ranged.

Summarizing, shock waves can be expected in systems with perfect caging, where the energy is mainly transported through the lattice in collisional sequences, but also energy will be transferred in off axis directions. The efficiency of the energy transfer by nearly elastic collisions of the lattice atoms leads to rather long-ranged shock waves.

1.4.2 Excitation of Coherent Phonons

In 1992 Zeiger et al. [55] published a theory for the initialization of long-living phonon modes, which was adapted later by groups like Lobad [56], Misochko [57] and several other groups [58]. Mostly the generation of phonon modes after optical excitation of a pure metal, semiconducting material or superconductors is investigated. Recently, Schwentner applied this mechanism to molecules embedded in a rare gas matrices [41].

The photoexcitation of electrons in materials like conductors or semiconductors leads to phase transitions and distortions in the lattice. This is due to the fact that the electrons are promoted from bonding to antibonding states. By this the equilibrium positions of the lattice atoms are changed so that they start to oscillate around their new equilibrium positions, inducing coherent phonons [59]. This is known as *displacive excitation of coherent phonons*, *DECP*. Applying this to our model of rare gas matrices containing impurities, the change in the wavefunction from the ground to an excited state with a different spatial distribution could lead to the same effect. Photoexcitation of the chromophore in the rare gas matrix leads to different equilibrium positions of the surrounding argon atoms and therefore oscillations of the lattice are induced.

The excitation of these modes is initiated by the excitation of the chromophore,

the oscillations will stay localized and thus the corresponding phonon mode can be observed for several picoseconds. Fig. 1.8 shows the experimental pump-probe



Figure 1.8: Pump-probe spectrum of I_2 in Krypton after excitation to the Bstate, (top), normalized (center) and for excitation to the energetically lower Astate,taken from [41]. Potentials see Fig. 1.15

spectrum of I₂ in Kr with $\lambda_{pump} = 530$ nm (B \leftarrow X), $\lambda_{probe} = 508$ nm (E \leftarrow B) and fluorescence recorded at 408 nm. For detailed discussion see [41] and the following section 1.5. Panel a) shows the measured spectrum. There is a decay on intensity in the time scale of 3 ps, which is due to the anharmonicity of the potentials and vibrational relaxation of the chromophore. The modulation in this part reflects the wavepacket motion. Both effects will be discussed in detail in the following section. From panel b), where the spectrum has been normalized to the mean value, it can be seen that underlying these effects due to the chromophore, there will be a second modulation, which is much more persistent and lasts for more than 9 ps. This modulation is independent of the excited state, as can be seen from panel c), which shows the same normalized spectrum after pumping to the lower lying A state. By comparison to the normal modes of krypton, this modulation is assigned to phonon modes, which were driven by the excitation process.

The detailed mechanism leading to this excitation of coherent phonons is not yet

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resolved and here theoretical simulations have to be performed.

1.5 Spectroscopy of Chromophore-Matrix Interaction

Due to the manifold of mechanisms for caging and/or energy distribution and their various influences on the dynamics of the system, experimental investigations of photodynamics in condensed phases become a challenge. For interpretation of the experimental results, simulations can be helpful. This section deals with some of the experimental techniques for resolving the solid state dynamics.

One of the most important methods for studying ultrafast dynamical processes is the femtosecond pump-probe spectroscopy. It presents an excellent tool for experimental studies of the underlying processes in condensed phase dynamics. Conventional excitation spectroscopy may lead to averaged results, where resolution of distinct effects is not possible due to solvent induced broadening of the peaks, or to spectra of a complex form, which will reflect the principal many-body behaviour of the system, but may not be able to reveal the underlying processes.

As an example, Fig. 1.9 shows the $B \leftarrow X$ excitation spectrum of Cl₂ in Ar,



Figure 1.9: Excitation spectrum of ${}^{35}Cl_2$ in Ar 1:3000, temperature 4 K. Taken from Bondybey (1976) [20]

publicated by Bondybey in 1976 [20]. The underlying rotational bands of the chlorine will collapse into the zero-phonon-band (ZPB), which will reflect the dynamics of the halogen molecule [4]. The spectrum shows sharp zero-phonon lines, accompanied by phonon-side-bands (PSB), indicating a coupling between

guest and host. For higher vibrational states of the chromophore, there will a sufficient increase of intensity of the PBS and it becomes difficult to distinguish between guest and host contribution. For systems with a more pronounced coupling between guest and host, the spectrum becomes rather broad and structureless.

The excitation spectrum shown here gives evidence of solute-solvent interaction, but contains no information about dynamical processes.

1.5.1 Pump-probe Spectroscopy



Figure 1.10: Pump-probe scheme: The pump pulse excites the wavepacket to the intermediate state. After some time delay a second pulse will probe this wavepacket to a higher, generally ionic state, from which laser induced fluorescense (LIF) is emitted. The measured intensity of this emission results in pump-probe spectra as shown in Fig. 1.11

A valuable tool for investigating the potential of the system, as well as the dynamics by taking 'snap-shots' at different time steps is presented by pump-probe spectroscopy. Dynamical processes, like vibrational relaxation, caging and recombination, can be mapped and interpreted, with help from the theoretical calculations. This section will be divided into two main parts. First the principles of pump-probe spectroscopy will be described and then the resolution of dynamical processes observed with pump-probe spectroscopy will be shown in an example.

Fig. 1.10 shows the scheme of pump-probe spectroscopy. The pump-pulse generates a wavepacket in an excited state. Due to the repulsive shape of the potential the wavepacket starts moving and reaches after some delay time t the probe region. Here the part of the wavepacket, which fulfills the excitation conditions - overlap of wavefunctions and energy ΔE - will be promoted to another excited state, usually one of the ionic states of the system. After nonradiative relaxation, laser induced fluorescence (*LIF*) will be measured.

Plotting the intensity of this fluorescence signal against the time delay will allow the analysis of the time-behaviour of the wavepacket, see Fig. 1.11. The intensity of the signal is inversely proportional to the momentum, because with increasing velocity the wavepacket will remain for a shorter time in the probe window and by this the probability for excitation to the ionic state is reduced. It has to be mentioned, that this relation only applies to the magnitude of the momentum [60], but on the other hand the direction of the momentum will be preserved during the probe excitation. Second, the intensity of the measured fluorescence will contain information about the coherence of the wavepacket. Decoherence will result in a decreasing modulation depth of the pump-probe sprectum. This loss of coherence is due to collisions with the environment, a process, in which the phase relation of the wavepacket is destroyed. In addition, if the wavepacket is already dispersed due to the anharmonicity of the potential, the probability of excitation in the probe event becomes smaller and the signal will be less intense.

Another important information extracted from pump-probe spectoscopy are the round-trip times T_1 of the wavepacket, see Fig. 1.11. It will pass the window after excitation and then a second time after recoil by the lattice. By keeping the probe energy fixed and only varying the pump wavelength, one can get information about the anharmonicity of the potential. Exciting higher vibrational states of the chromophore will result in longer round-trip times, due to this anharmonicity. This is depicted in Fig. 1.12. The round trip time of the highest vibrational state is longer than for the lowest excited one. The splitting of the peaks because of this inward and outward motion of the wave packet will vanish at the turning point and λ / nm 600 550 500

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this can be extracted from the spectra by keeping the pump wavelength fixed and changing the proper wavelength. In this sense the mean shape of the potential will be reflected in the pump-probe experiments.

Determining the round frip times σ_1 , another difficulty is arising. Taking just the difference between the peaks as signed to outward and inward motion would not reflect the properties of the properties of the peaks as signed to outward and inward motion would not reflect the properties of the excited, see Fig. 1.12, depending on the bandwidth of the pump pulse and this will result in a distribution ΔE_{win} . The wavepacket will start moving outwards until it reaches the probe window. Here again a band of vibrational states will be excited to the final ionic state, depending on the ΔR_{win} . Now due to the anharmonicity of the potential probably only few (in Fig. 1.12 only the upper two) vibrational levels will be probed. The resulting vibrational period will not reflect the correct round-trip time for the center of the wavepacket, because the lower parts of the excited vibrational levels in the pumped state, which have the main contribution for the excitation with the initial wavelength, will not con-



Figure 1.11: Pump-probe spectra of I_2 in Kr. Left panel: fixed probe and different pump wavelength, right panel: fixed pump and different probe wavelength. T_1 (left panel) means round-trip time of the wavepacket. The dashed lines connect the times for the passages through the probe windows, \rightarrow and \leftarrow indicate the direction of momentum (outwards or inwards)

tribute. On the other hand, moving to higher energy for the probe pulse will shift the window to smaller distances and now the less energetic parts of the wavepacket will gain influence and the time T_1 is reduced because of the shorter vibrational period in the anharmonic potential. To reduce the errors for the T_1 one has to apply λ_{probe} to the turning point of each λ_{pump} .

From the classical point of view, excitation will lead to trajectories with different



Figure 1.12: Potential diagram for the pump-probe mechanism with respect to the distribution to the vibrational states of the excited state. The pump pulse populates a certain bandwidth of vibrational levels. Subsequently, the probe pulse determines, which of these levels are probed.

excess energy. Those with the highest excess enery will have the highest kinetic energy or momentum. They travel fast and thus the time they remain in the probe window will be shortened, reducing the probability for excitation by the probe pulse. In this case the weight of the trajectories with less energy will by overweighted and the time T_1 will be too small. If the probe window is too high in energy, the statistical average of the trajectories will not reach the window and only the energetical higher trajectories will be probed and by this the time T_1 will get too large.

It has to be emphasized, that the measured potentials are alway mean potentials, because the potential energy of the chromophore will be influenced by the lattice dynamics. Pump-probe spectroscopy gives always difference potentials in the sense that the excitation conditions have to be fulfilled. Strong interaction with the environment may lead to a broadening of the spectrum and the determination of round-trip times and the resolution of the processes becomes difficult or the probe window may be shifted due to motion of the lattice atoms.

1.5.1.1 Vibrational Relaxation

Connected to the round trip times mentioned before, information about vibrational relaxation processes can be determined from pump-probe spectroscopy. In his Ph.D. Thesis, M. Bargheer describes two different ways of determining the vibrational relaxation kinetics [40], depending on the system and the resolution of the spectra. Fig. 1.13 shows determination of energy relaxation schematically. The wavepacket is pumped to an electronic excited state, where it will start to dissociate, as described before. Given enough kinetic energy, the fragments of the molecule will hit the cage atoms, resulting in an energy loss of the chromophore and thus to vibrational relaxation by transferring momentum to the matrix atoms. For well resolved wave packet oscillations, like in the case of iodine in krypton,



Figure 1.13: Scheme for detecting the rate of vibrational relaxation k_{rel} , compare to equation 1.1

the round trip times T_n , discussed above, will indicate the anharmonicity of the potential and can be connected to the mean energy of the potential. By this rates for the energy relaxation in time, dE/dt can be determined.

In other cases only few oscillation periods can be observed, which is the case for molecular chlorine in argon matrices. Here the time for the energy relaxation from the initial E_{pump} to the measured energy E_{probe} can be determined from the maximum of the signal envelope, compare to Fig. 1.13. In the classical picture, the maximum of the measured signal indicates probing at the turning point of the potentials. At this points, the molecular fragments will have no kinetic energy, and since the measured fluorescence is inversely proportional to the velocity of the particles, the signal will reach a maximum. For the quantum picture this would mean a stationary wave function at the turning point, resulting in a high Franck-Condon overlap and a high transition probability for the probe. The initially high velocity of the wave packet will be lost by collisions with the matrix atoms. This leads to an increase of the measured fluorescence. After reaching the maximum by probing at the turning point, the wavepacket will relax further, loosing energy and by this leaving the probe window. In this picture the times τ_m , connected to the energy loss,will determine the energy relaxation rates. The ratio between



Figure 1.14: Experimental determined rates k_{rel} for the systems I₂/Kr, Cl₂/Ar, ClF/Ar

the probe energy, determined by the probe pulse, and the time delay between the maxima of the measured signals will give the difference of energy over the time

difference, thus determining the relaxation rate.

$$\frac{dE}{dt} = \frac{E_i - E_j}{t_i - t_j} \tag{1.1}$$

For the investigated dihalogens in rare gas environments, exponential relaxations rates $k_r el = dE/dt$ could be determined, which indicates a large energy loss in the first oscillation periods. When the wave packet is relaxed nearly to the bottom of the potential of the bound excited state, the rate constants will get small, which could reflect only a weak interaction with the environment at low energies. This will be discussed in detail in the chapter 6.8. Fig. 1.14 shows the measured relaxation rates for the systems I₂/Kr, ClF/Ar and Cl₂/Ar.

Pump-probe spectra in condensed phases show some important features. The direct collision with the host atoms will lead to an energy loss of the guest molecule and it will therefore relax energetically. Due to the anharmonicity of the potential, the vibrational frequency and the envelope of the signal will be changed. Second, the energy flow between host and guest atoms will lead to a broadening of the peaks because of decoherence. The wavepacket, which is focussed at the beginning, will spread after some time because of the anharmonicity of the potential and of the disturbances from the surrounding atoms.

The interaction between the guest and host dynamics has been investigated by several groups. The probably best known system in this respect is iodine in rare gas matrices. Here several important features and effects were observed by pumpprobe spectroscopy, but still not all of these could be explained by theoretical investigations. The aim is to give a detailed description of the guest-host interactions and by this to resolve the spectroscopic details.

1.5.2 Example: I_2 in Kr

One very clear demonstration of experimental evidence for the dynamics after excitation of iodine in krypton to the B-state and the difficulties arising by interpreting the spectrum is given by Zadoyan and Apkarian [60]. The spectrum is shown in Fig. 1.16, potentials in Fig. 1.15

The first double peak, labeled as 1 is resulting from the outgoing wave. It is splitted to an earlier, more intense part and a later one, which is less intense.



Figure 1.15: Potential energy curves of the system I_2 in Kr, calculation see Batista [73].

This reflects outwards and inwards motion of the wavepacket as explained in section 1.5.1. The interesting point here is the relative intensity of the peaks. After excitation to the repulsive B-state, the fragments will start to dissociate, gaining velocity. This would mean that the wavepacket stays for a shorter time in the probe window, and a signal with comparatively small intensity has to be expected. After passing the probe window, the collision with the lattice atoms will happen. By this collision the iodine would loose a large amount of its kinetic energy to the collision atom of the lattice. The molecule will be slowed down and therefore one would expect an increase of intensity for the peak of the returning wave, because in this case the wavepacket will remain for a longer time in the probe window. Quite the opposite is reflected in the spectrum, the first of this double peak being more intense than the second one. One interpretation for the reduced intensity of the second peak is given by Apkarian and coworkers [60]: since the population



Figure 1.16: Pump-probe spectrum of ${}^{1}\Sigma_{g}^{+} \rightarrow {}^{3}\Pi_{0u}$ excitation of I_{2} in Kr, taken from [60]

remains on the B-state, the probe window is shifting due to the modified geometry of the solvation shell after the collision incident. The ionic state, which is probed, is strongly solvated and would react notably to the changed position of the solvent atoms. Since only difference potentials are measured in pump-probe spectroscopy, this would mean that a different ionic state is probed. In addition, the next resonance (label 2) only forms a single peak and there will be no resolution of the outgoing and returning wavepacket. This effect gives evidence of a shifting of the probe window to the turning point of the potential.

Peak number 3 is reflecting the same effect as the first double peak. It is shorter than his neighbours and shows a small shoulder. Here two different mechanisms are working. First the reduction of intensity can be assigned to the gain of velocity at that time. Comparing to a different experiment including pumping to the A state of iodine, there is evidence that at this time the guest molecule is accelerated by interaction with the cage and energy from the lattice is transferred back to the chromophore. The momentum transferred to the cage during the dissociation of the chromophore is stored locally and is now given back to the molecule. This would explain the change in intensity of this signal, but not the distortion in form of a small shoulder. This could be explained the same way as above, namely the

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probe window changing. This would include a time dependence of the difference potential for the probe excitation, due to lattice dynamics of the system. Again, here simulations are important to resolve the shaping and frequency of the measured signals and to give a correct interpretation of the spectrum.

Peak 4 denotes the following progression of signals. The molecule has now reached the bound part of the B-state potential and will relax vibrationally. The period of the oscillations start at ca. 450 fs and reaches the limit of 350 fs prior to moving out of the probe window. This fits well to the gas phase harmonic period of 300 fs for iodine and can be connected to the chromophore.

After approximately 4 ps a different trend sets in. The oscillations have a longer period around 700 fs and are clearly not resulting from the chromophore. On the other hand they fit nicely to the periods found for the phonon modes of krypton and are therefore designated to lattice vibrations. In this case the harmonic modulation of the lattice atoms will result in a harmonic motion of the probe window via shifting of the ionic states, so that it will be in and out of resonance with the same frequency as the responsible phonon mode.

Which of the atoms in the vicinity of the chromophore is responsible for the elastic response of the cage and the back-transfer of momentum which modulates peak 3 or which of the caging atoms are responsible for the phonon mode from the band number 5 is not yet resolved, but it becomes clear that there is a necessity to perform simulations which could explain the behaviour of the system.