Ultrafast Photo-induced Reaction Dynamics of Small Molecules

BY

MALIN KADI
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Abstract

The main focus of this thesis is the investigation of the dissociation dynamics of aryl halides using femtosecond pump-probe spectroscopy. In the monohalogenated aryl halides, iodo-, bromo- and chlorobenzene, the rate of dissociation following excitation at 266 nm in the gas phase increased with increasing mass of the halogen atom. This process was assigned to predissociation of the initially excited singlet (π, π*) state via a repulsive triplet (n, σ*) state due to spin-orbit interaction. In addition to the predissociative mechanism, a direct dissociation channel was observed in iodobenzene. The rate of the predissociation in bromobenzene was found to be faster in the condensed phase than in the gas phase, which can be explained by solvent-induced symmetry perturbations. Ab initio calculations of the potential energy surfaces of the ground state and several low lying excited states in bromobenzene have been performed in order to verify the suggested mechanism. Substituting one of the hydrogen atoms in bromobenzene affected the predissociation rate significantly. In o-, m- and p-dibromobenzene the predissociation rate increased with decreasing distance between the bromine atoms in accordance with an increased spin-orbit interaction introduced by the bromine substituent. The fastest predissociation rate was observed in 1,3,5-tri bromobenzene. With chlorine and fluorine substitution, inductive and conjugative effects were found to be of importance. In the o- and m-isomers of the dihalogenated aryl halides, an additional faster dissociation channel was observed. Guided by ab initio calculations of the potential energy surfaces in the dibromobenzene isomers, we ascribed the fast dissociation pathway to predissociation of an initially excited triplet state. Upon methyl group substitution in bromobenzene, the decreased lifetime of the initially excited state was attributed to an increased density of coupled states.

Another system which has been studied in the condensed phase is diiodomethane. Using Car-Parrinello molecular dynamics simulations we observed a prompt dissociation and subsequent recombination to the isomer, iso-diiodomethane, in acetonitrile solution. Vibrational wavepacket dynamics in the C (Σ') state of NaK were studied using a direct ionization probing scheme. A simple analytical expression for the pump-probe signal was developed in order to see what factors that govern direct ionization of the vibrational wavepacket. Our experimental data was consistent with a photoionization transition dipole moment that varies with internuclear distance.

Keywords: pump-probe spectroscopy, reaction dynamics, photodissociation, aryl halides, spin-orbit coupling, ab initio calculations, molecular dynamics, vibrational wavepackets

Malin Kadi, Department of Physical Chemistry, Box 579, Uppsala University, SE-75123 Uppsala, Sweden

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This thesis is based on the following papers, which will be referred to in the text by their Roman numerals.


V. Liu, Y-J., Persson, P., Kadi, M., Karlsson, D., Karlsson, H O., Davidsson, J., Lunell, S. The photodissociation of bromobenzene, dibromobenzene and 1,3,5-tribromobenzene. (manuscript)

VI. Odelius, M., Kadi, M., Tarnovsky, A N., Davidsson, J. Photodissociation of diiodomethane and recombination into iso-diiodomethane in acetonitrile solution studied with ab initio molecular dynamics simulations. (manuscript)

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Comments on my participation

**Paper I.** I performed all the experimental work and most of the data analysis. Wrote most of the paper.

**Paper II.** I performed a few experiments. Proof-read the paper

**Paper III.** I took the initiative to study the systems and planned the experiments. Performed all the experimental work together with one of the co-authors. Wrote the paper.

**Paper IV.** I took the initiative to study the systems, planned and performed all the experimental work and data analysis. Wrote the paper.

**Paper V.** I performed parts of the analysis of the calculations, participated in scientific discussions and wrote parts of the paper.

**Paper VI.** I performed parts of the simulations, participated in scientific discussions and wrote parts of the paper.

**Paper VII.** I performed all the experimental work together with one of the co-authors and parts of the calculations. Participated in scientific discussions and proofread the paper.
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### Abbreviations

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<th>Abbreviation</th>
<th>Full Description</th>
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<tbody>
<tr>
<td>BBO</td>
<td>Barium borate</td>
</tr>
<tr>
<td>CASSCF</td>
<td>Complete active space self-consistent field</td>
</tr>
<tr>
<td>CPMD</td>
<td>Car-Parrinello molecular dynamics</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width half maximum</td>
</tr>
<tr>
<td>IC</td>
<td>Internal conversion</td>
</tr>
<tr>
<td>ISC</td>
<td>Intersystem crossing</td>
</tr>
<tr>
<td>IVR</td>
<td>Intramolecular vibrational redistribution</td>
</tr>
<tr>
<td>LIF</td>
<td>Laser induced fluorescence</td>
</tr>
<tr>
<td>MB</td>
<td>Molecular beam</td>
</tr>
<tr>
<td>MPI</td>
<td>Multiphoton ionization</td>
</tr>
<tr>
<td>MS-CASPT2</td>
<td>Multi-state multi-reference 2nd order perturbation theory</td>
</tr>
<tr>
<td>PES</td>
<td>Potential energy surface</td>
</tr>
<tr>
<td>PTS</td>
<td>Photofragment translational spectroscopy</td>
</tr>
<tr>
<td>ROKS</td>
<td>Restricted open-shell Kohn-Sham method</td>
</tr>
<tr>
<td>TOF-MS</td>
<td>Time of flight mass spectrometer</td>
</tr>
<tr>
<td>TOPAS</td>
<td>Travelling wave optical parametric amplification of superfluorescence</td>
</tr>
<tr>
<td>VR</td>
<td>Vibrational relaxation</td>
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1 Introduction

The breaking and formation of chemical bonds, the most fundamental process in chemistry, was until the mid 1980:s never studied in real time. Atoms move on the timescale of 1 km/s and the relevant distance over which bonds are broken and formed are some Angstroms \((10^{-10} \text{ m})\), which means that the lifetime of the activated complex over which the reaction proceeds is shorter than 100 femtoseconds \((\text{fs})\). Hence, in order to study these transition structures in real time, a time resolution of the experiment on the femtosecond timescale is required.

Ever since the advent of the first laser in 1960, new lasers with shorter pulses have been developed and opened up the possibility to study faster chemical processes in real time. The first laser with femtosecond pulses was realized in 1981. Ahmed Zewail (Caltech, Pasadena, USA) was one of the first who applied femtosecond lasers to study ultrafast reaction dynamics. In 1999 he was awarded the Nobel Prize in chemistry for his achievements.

The methodology used to investigate the ultrafast dynamics is the so-called pump-probe technique. In this technique, a short laser pulse, the pump, serves to initiate the reaction and a second laser pulse, the probe, is used to monitor the accompanying chemical changes. In combination with quantum mechanical calculations important information about activated complexes and molecular structures can be extracted. As the time resolution in pump-probe experiments is limited by the pulse width, reactions proceeding on the fs time scale can be measured using fs laser sources.

In this thesis the ultrafast reaction dynamics of small molecules have been investigated. The main focus is on the dissociation dynamics of aryl halides, which was studied employing the pump-probe technique. Quantum mechanical calculations have been performed in order to obtain a more complete picture of the dynamics of these compounds.
2 Experimental Method

The experimental technique employed in the work presented in this thesis for investigating the ultrafast dynamics is femtosecond pump-probe spectroscopy. Experiments have been performed both in the gas phase, i.e. in a molecular beam (MB), and in the condensed phase.

The following chapter contains a description of the pump-probe technique and the experimental setups.

2.1 The Pump-Probe Technique

In the pump-probe technique a femtosecond (fs) laser pulse is divided into two fractions using a beam splitter. One part, the pump pulse, serves to initiate the reaction and the other part, the probe pulse, is used to monitor the reaction by for example measuring transient absorption, laser induced fluorescence or ion yield following multiphoton ionization (MPI). In pump-probe experiments the time resolution is usually limited by the time duration of the laser pulse.

In our experiments the pump pulse travels a constant path to the sample, whereas the path length of the probe pulse is changed in a variable delay line, as schematically illustrated in Fig. 2.1. The pump and the probe pulses are focused and spatially overlapped in the sample (e.g. a molecular beam in Fig. 2.1). At time zero, the pump and the probe pulses have traveled exactly the same distance before reaching the sample. Increasing the travel distance of the probe pulse will induce a time delay. Hence, the reaction is monitored at different times after initiation.

In the MB experiments presented in paper I, III, IV and VII the reaction dynamics was probed by multiphoton ionization (MPI) followed by ion detection. In the condensed phase experiments in paper II, probing of the dynamics was accomplished by measuring transient absorption.
2.2 The Femtosecond Laser System

The femtosecond laser system consists of a mode-locked Ti:Sapphire oscillator (Mira 900-F, Coherent radiation) pumped by an Ar-ion laser, generating pulses at 800 nm (FWHM=12 nm). The temporal width of the pulses is about 80 fs and the repetition rate of the oscillator is 76 MHz. The pulses are amplified in a Ti:Sapphire regenerative amplifier (Quantronix 4800 fs-3k) pumped by a Q-switched Nd-YLF laser with a repetition rate of 1 kHz. Before the seed pulses enter the amplifier system, the pulses are temporally stretched in order to avoid to high intensities that could damage the optics in the laser. After the amplification stage the pulses are recompressed to a temporal width of about 120 fs. The energy content of the amplified pulses is 800 µJ and the spectral width 10 nm. The output pulses are divided into two parts using a beam splitter. One part is used to seed an optical parametric amplifier (TOPAS, traveling wave optical parametric amplification of superfluorescence) and the other part is normally used to generate the pump pulses as discussed below.
In the TOPAS (Light Conversion Ltd.) different frequencies are generated through interaction of three photons in a non-linear crystal. A pump pulse at frequency $\omega_3$ generates two new waves at frequencies $\omega_1$ (signal) and $\omega_2$ (idler) according to the phase matching condition:

$$\omega_3 = \omega_1 + \omega_2$$

In the experiments presented in this thesis, the pump and the idler was mixed in a second non-linear crystal, yielding a tunable output in the wavelength range 530-620 nm.

![A schematic illustration of the femtosecond laser system used in the gas phase experiments.](image)

**Fig. 2.2.1** A schematic illustration of the femtosecond laser system used in the gas phase experiments.

### 2.2.1 The pump-probe setups

In paper I, III and IV, the TOPAS was tuned to generate pulses at 540 nm. These pulses were used for probing. The pump pulses were generated from the 800 nm output pulses from the regenerative amplifier employing two BBO (Barium borate) crystals in a home-built tripling device, as schematically illustrated in Fig. 2.2.2.

In the first BBO crystal (1 mm thick), the horizontally polarized 800 nm pulse is frequency doubled generating a vertically polarized pulse at 400 nm. The 400 nm pulse is reflected at a dichroic beam splitter
(BS) and lead to the second BBO crystal (0.4 mm thick), whereas the residual 800 nm is transmitted through the beam splitter into a variable delay line before reaching the crystal. The delay line enables the adjustment of the temporal overlap of the two pulses in the second BBO crystal. The polarization of the 800 nm pulse is rotated 90 degrees using a $\lambda/2$-plate so that the polarization of both the 800 nm and 400 nm pulses is vertical. Then, when the two pulses are spatially overlapped in the second BBO crystal, a pulse at 266 nm is produced through sum-frequency generation.

As the output pulses from the Ti:Sapphire oscillator can be tuned between approximately 785 nm and 825 nm, pump pulses between 262 nm and 275 nm can be generated by frequency tripling.

Fig. 2.2.2 A schematic illustration of the home-built frequency tripling device.

In the pump-probe experiments the approximate temporal overlap (time zero) of the pump and the probe pulse was found by overlapping the residual 800 nm pulses from the TOPAS and the tripling device in a BBO crystal. At time zero, the cross correlation between the two pulses generates light at 400 nm. A coarse spatial overlap between the pump and probe pulses was achieved by adjusting the two beams through a small pinhole ($\varnothing = 0.2$ mm) outside the MB apparatus. Then, the overlap was finely adjusted by optimizing the ion signal.

A Berek polarization compensator was placed in the path of the pump pulse so that the plane of polarization could be varied. In most of the experiments, the relative polarization of the pump and the probe pulse was set at magic angle ($54.7^\circ$).
In paper VII, a one-colour pump-probe setup was used and the pump and probe pulses were generated by dividing the output from the TOPAS ($\lambda = 529$ nm) into two fractions with a beam splitter. Also in these experiments magic angle conditions were employed.

2.3 The Molecular Beam Apparatus

The molecular beam (MB) apparatus consists of two diffusion pumped vacuum chambers joined by a small opening ($\varnothing = 3$ cm). The molecular beam source is located in the first chamber, and the second chamber contains the time-of-flight mass spectrometer (TOF-MS). A low pressure ($10^{-6}$ mbar) in the detection chamber is assured by differential pumping of the two chambers.

The MB apparatus is schematically illustrated in Fig. 2.3.1. In the MB source the sample is loaded to the reservoir. Due to the pressure difference, the molecules diffuse through the exit pipe and expand through a 0.1 mm aperture. At the employed conditions, i.e. pressure difference and aperture size, the beam is effusive or only slightly expansion cooled.

The molecular beam enters into the detection chamber containing the TOF-MS. The propagation direction of the beam coincides with the TOF-MS axis.

Fig. 2.3.1 A schematic view of the molecular beam apparatus (not to scale).
The ion optics in the TOF-MS consists of three parallel plates, with the potentials: +400 V, +280 V and 0 V. In the region between the first and the second plate, the pump and the probe beams are focused and spatially overlapped in the molecular beam. The ions formed by photoionization with the probe pulse are accelerated between the first and the third plate and traverse thereafter a flight distance of about 30 cm under field-free conditions between the third and the fourth plate. After passing the fourth plate, they enter into the ion detector.

The ion detector consists of a dynode, a scintillator and a photomultiplier, an arrangement that assures a reliable setup with high sensitivity. The potential of the dynode was typically –9 V and the potential of the scintillator plate was held at 1.2 kV. In Fig. 2.3.2 an example of a TOF-MS spectrum can be seen.

Fig. 2.3.2 A time of flight mass spectrum of bromobenzene recorded with a single laser pulse at 266 nm.

2.4 Data Acquisition

In the pump-probe experiments, the signal from the desired ion species was collected by a boxcar integrator and averaged over typically 10 000 laser shots at each time delay.

Furthermore, a mechanical shutter was placed in the path of the probe pulse, so that the contribution to the ion signal from only the pump pulse could be measured. This single beam contribution reflects

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1 A lower potential difference between the first two plates, where the photo-ions are formed, ensures a good mass resolution in the spectrum.
fluctuations in the laser intensity and variations in the density of molecules in the molecular beam.

In the NaK experiments two boxcars were used so that the NaK$^-$ and K$^+$ yield could be measured simultaneously. The K$^+$ trace was then used to accurately determine time zero since multiphoton ionization of K atoms is enhanced when the pump and probe pulses overlap temporally in the MB. At time zero a distinct peak, corresponding to the cross-correlation of the pump and the probe pulse, could be observed.

2.4.1 Data Analysis

The pump-probe signal and the signal from only the pump pulse (pump signal) do not necessarily have the same dependence on the laser intensity. Therefore, it is not always possible to properly correct for laser fluctuations by division of the pump-probe signal with the pump signal. However, as the pump signal is also present in the pump-probe signal, there is no additional error introduced by subtracting the pump signal from the pump-probe signal, even though they are not linearly dependent.

Hence, in our experiments the pump signal was generally subtracted from the pump-probe signal and kinetic traces where the pump signal was drifting have not been used.

Data analysis was performed using the Microcal Origin™ software.

2.5 Transient Absorption Measurements

In femtosecond transient absorption measurements a pump pulse is used to initiate the reaction, and the probe pulse is used for monitoring the chemical changes by measuring the accompanying changes in absorption (transient absorption). This experimental technique was used in paper II$^2$.

The pump pulses at 266 nm were generated by frequency tripling the fundamental output pulses at 800 nm from a regenerative amplifier. A

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$^2$ These experiments were performed in the femtosecond lab at the Department of Chemical Physics, University of Lund.
white light continuum, either around 400 nm or 800 nm, was generated in a sapphire plate and used for probing. The pump and the probe pulses were spatially overlapped in a 1 mm flow cuvette. After the cuvette, a monochromator was used to select the desired analyzing wavelength and the transmission intensities were measured with photodiodes.

In order to measure the transient absorption every second pump pulse was blocked using a mechanical chopper. Hence, the transmitted probe pulse intensity was measured both when the pump was on and when it was off. The difference corresponds to the transient absorption changes accompanying the reaction initiated with the pump pulse. Also, in order to correct for fluctuations in the laser intensity, a part of the probe light was split off before the sample and used as a reference beam. The transient absorption was then calculated using the following equation:

\[
\Delta A = \log \left( \frac{I}{I_{\text{ref}}} \right)_{\text{pump off}} - \log \left( \frac{I}{I_{\text{ref}}} \right)_{\text{pump on}}
\]  

Eq. 2.1
3 Reaction Dynamics in Molecular Beams

The earliest investigations of reaction dynamics were performed in crossed molecular beams (MB)\(^1\). Important information about the mechanism of bimolecular reactions could be extracted from these experiments. By analyzing the angular and translational energy distributions of products following different collision angles and collision energies, the potential energy surface of the reaction as well as the partitioning of available energy into different degrees of freedom of the product could be determined.

The first MB:s used were effusive beams, which are formed by allowing molecules to expand through a narrow pinhole into a lower pressure region. In effusive beams, the molecules are not much expansion cooled and the temperature of the molecules is about the same as the temperature of the source. Later on it was recognized that if molecules were expanded with a carrier gas, typically helium or argon, from a higher pressure through a small aperture into a lower pressure side, a beam of very cold molecules was formed. In this supersonic beam the translational, rotational and vibrational energies of the molecules are extremely low\(^2\). Due to this low temperature, the individual rotational levels can be resolved in the spectrum of larger molecules\(^3\). Moreover, using argon gas in the expansion allows the formation of clusters. As the cluster size can be varied by varying the beam conditions, the dependence of a solvent on the reaction dynamics can be explored in a controlled way. Energy transfer to solvent molecules or in-cage recombination of photofragments following dissociation can then be investigated. Also, in weakly bonded complexes bimolecular reactions can be studied with femtosecond spectroscopy.

Furthermore, by using laser pulses at a certain wavelength for excitation, the initial state of a reagent molecule can be selected. By varying the initial state instead of measuring the rate constant of the reaction, which is an average over reactions with reagents in different
initial states, state-resolved dynamics can be measured\(^4\). Also, excitation of a specific vibrational state permits the investigation of intramolecular vibrational energy redistribution (IVR). The process of IVR has been extensively studied in the gas phase because of its importance in mode-selective chemistry\(^5, 6, 7, 8\).

With the use of current femtosecond lasers the time resolution is sufficient to study vibrational wavepacket dynamics. Since the dynamics of a vibrational wavepacket directly relates to the motion of atoms, one can learn about how chemical reactions proceed and also how to steer and control the reaction. Moreover, from these experiments it is also possible to determine the potential energy surface (PES) of a molecule by different inversion procedures\(^9, 10, 11\).

Alkali diatomic molecules have often been used for investigations of vibrational wavepacket dynamics\(^12, 13, 14, 15\). In paper VII in this thesis we have chosen to study the vibrational wavepacket dynamics in the C \((^1\Sigma^+)\) electronic state of the NaK molecule.

Another important field in reaction dynamics is the study of half-collisions, i.e. photodissociation reactions. Since the 1970:s photodissociation reactions have been investigated in molecular beams using the technique of photofragment translational spectroscopy (PTS). The systems investigated in this thesis, i.e. alkyl halides and aryl halides, have been extensively studied using PTS.

The following section contains a description of the PTS technique and a brief survey of previous experiments relevant in the discussion of the results from our experiments.

### 3.1 Photofragment Translational Spectroscopy (PTS)

A technique that has been extensively used to study the photodissociation dynamics of aryl halides in molecular beams is photofragment translational spectroscopy (PTS). With this technique, the partitioning of available energy into translational and internal degrees of freedom is measured, and the number of different dissociation channels and their relative probability and rate is determined. Also, if the spatial distribution of photofragments is measured, the direction of the transition dipole moment and the approximate timescale of dissociation can be deduced\(^16, 17, 18\).
In this technique, polarized light is used to photodissociate the molecules and the resulting photofragments are ionized by electron bombardment. Thereafter the translational and angular distribution of photofragments is measured in a time of flight mass spectrometer (TOF-MS).

The angular distribution of photofragments is given by\(^{19, 20}\)

\[ I(\theta) = \frac{1}{4\pi} [1 + \beta P_2(\theta)] \tag{3.1} \]

where \(\theta\) is the angle between the recoil direction and the plane of polarization of the dissociating laser pulse. \(P_2\) is the second order Legendre polynomial and \(\beta\) is the anisotropy parameter. \(\beta\) gives information about the direction of the transition dipole moment and the dissociation time. For a prompt dissociation, i.e. a dissociation that is faster than the rotational correlation time, \(\beta = 2\) for a parallel transition (the transition dipole moment is parallel to the dissociation direction) and \(\beta = -1\) for a perpendicular transition. For a dissociation that is much slower than the rotational correlation time the value of \(\beta\) will be close to zero.

The first experimental studies on the photodissociation dynamics of aryl halides were performed by Bersohn and coworkers\(^{21, 22}\). Using PTS they determined \(\beta\) for a series of aryl iodides and bromides and could determine approximate dissociation times. As the lifetime of the excited states were two orders of magnitude longer in aryl bromides than in aryl iodides they suggested that predissociation due to intersystem crossing plays a central role in the photodissociation of these compounds. Ever since these pioneering experiments, the photodissociation dynamics of aryl halides have been extensively studied, mainly using PTS. In PTS experiments by Zhang et al. the photodissociation of bromobenzene following excitation at 266 nm were investigated\(^{18}\). Only one translational energy distribution could be observed, indicating that the dissociation occurs via just one channel. Also, the value of the anisotropy parameter \(\beta\) (-0.7) implied that the dissociation is a fast process and that the transition dipole moment is perpendicular to the dissociation coordinate. They proposed two possible dissociation mechanisms, the first one a direct
dissociation due to $\sigma^*\rightarrow\pi$ excitation in the C-Br bond and the second a fast predissociation involving intersystem crossing (ISC).

With the same technique, chlorobenzene has also been observed to dissociate via only one pathway following excitation at 266 nm$^{23}$. It was suggested that the excited state molecules internally convert to the ground state and dissociate via highly excited vibrational levels, a process which is normally referred to as a hot molecule mechanism. Employing a higher energy for excitation ($\lambda_{\text{exc}} = 193$ nm), chlorobenzene was found to dissociate via three different channels. These were assigned to a direct dissociation, predissociation via vibrationally excited triplet levels and a hot molecule mechanism$^{24}$.

In other PTS experiments by the group of El-Sayed molecular rotation has been used to clock the rate of energy redistribution in iodobenzene following excitation at 304 nm$^{16,17}$. Two different dissociation channels were observed, a direct and a predissociative, in agreement with the observations made by Zewail et al$^{25}$. The rate of energy redistribution was found to occur on the same timescale as the predissociation, and a range of dissociation times were therefore observed.

Following these experiments, the PTS technique has been applied to investigate the effect of substituents on the photodissociation dynamics of aryl halides. Most experiments have been performed on chlorobenzene, but there have also been a few experiments on bromobenzene. These experiments are discussed in chapter 6.
Reactions occurring in the solution phase are much influenced by the surrounding solvent molecules. Solute-solvent interactions might cause the potential energy surfaces to shift in energy and thereby affect the coupling between different potential energy surfaces. The surrounding solvent molecules can also break the symmetry of the solute and the transition rates between different states can therefore be increased.

Moreover, if reactants or products are vibrationally excited, the excess excitation energy can be transferred to the vibrational and translational modes of the solvent molecules in a process referred to as vibrational relaxation (VR). In a polyatomic molecule, if the vibrational energy is initially localized in a specific vibrational mode, the vibrational energy will eventually redistribute over all vibrational degrees of freedom. This process is known as intramolecular vibrational energy redistribution (IVR). Even though IVR occurs within the molecule the process can be facilitated by the solvent. The rates of VR and IVR can be vastly different and depends for example on the size of the molecule, excess excitation energy and the polarity of the solvent. In for example experiments on I$_2$ it was found that vibrational relaxation is faster at higher excess energies where the spacing between the vibrational levels is closer$^{26}$.

One of the more important differences between photodissociation in the condensed phase compared to the gas phase is the ability of the solvent to prevent the photofragments from separating. In collisions with solvent molecules the fragments loose kinetic energy and recombination to the parent molecule or an isomer is possible. This cage effect has been extensively studied for I$_2$$^{26, 27, 28, 29, 30, 31}$. Due to the spherical symmetry of I$_2$ and the fact that it recombines to the parent molecule it is one of the simplest dissociation and recombination reactions to study. With larger molecules the recombination is more complicated due to restrictions on fragment
orientation and the possibility of recombination to either the parent molecule or an isomer. Isomer formation has been experimentally observed upon photodissociation of alkyl halides, such as CH$_2$I$_2$,$^{32}$ CH$_2$IBr$^{33}$ and CH$_2$ICl$^{34}$.

Work in this thesis on condensed phase dynamics includes the MD simulation on CH$_2$I$_2$ in acetonitrile solution where we have seen how the cage effect leads to formation of the isomer, CH$_3$I-I, and the pump-probe experiments on the photodissociation dynamics of bromobenzene in solution, where we observed how the solvent environment facilitates intersystem crossing.
5 Dissociation Reactions

Dissociation reactions are the most fundamental reactions to be studied and constitute the main topic of this thesis. In this chapter a description of three different classes of dissociation reactions will be given, all of them which have been observed in aryl halides.

5.1 Direct Dissociation

The simplest among the dissociation reactions are the direct dissociations; the breaking of a chemical bond on a repulsive potential energy surface. Following light absorption, the energy of the system is minimized by breaking of a bond and the excess excitation energy, which is available after the dissociation is converted into translational energy. In PTS experiments, direct dissociations are recognized by a large fraction of available energy that is partitioned into translational energy and a high spatial anisotropy of the photofragments.

Fig. 5.1 An example of a direct dissociation, the breakage of the C-I bond in CH$_2$I$_2$ on a repulsive potential energy surface.
The time required to break a bond in a direct dissociation is determined by the movement of a wavepacket on the repulsive potential energy surface and depends accordingly on the slope of the potential and the mass of the fragments. The timescale of direct dissociations is usually on the order of a couple of tens to hundreds of femtoseconds.

The ICN bond dissociation was the first one experimentally studied. In these experiments the rise and decay of the transition species $I\cdots CN^*\dagger$ and a delayed appearance of the free CN product was observed. The dissociation time was determined to 200 fs and the transition state was found to exist for only 50 fs.

Later on, direct dissociations have been observed in alkyl halides, for example CH$_3$I, CH$_2$I$_2$, C$_2$H$_5$I and CH$_2$BrI, when excited in their A-band. Also, a direct dissociative mechanism was found to occur in iodobenzene following excitation at 278 nm and 266 nm.

5.2 Predissociation

A more complex class of dissociation reactions is the predissociations. In systems experiencing predissociation, excitation is to a bound electronic state, which dissociates due to coupling with another state. Generally predissociations are slower than direct dissociations, resulting in photofragments with less translational energy and a lower spatial anisotropy in PTS experiments.

Predissociations have been classified in three different categories by Herzberg: predissociation by electronic interaction, predissociation by vibration and predissociation by rotation.

*Predissociation by electronic interaction:* In this type of predissociation, which is the most common, a bound electronic state is crossed with the dissociative continuum of another electronic state. Various types of interactions can mediate the coupling between the two states, for example non-adiabatic interaction between the adiabatic surfaces, spin-orbit interaction, electron-rotation interaction, hyperfine interaction and interaction induced by external fields. Very fast predissociation can occur when two electronic states of the
same symmetry approach each other or if the spin-orbit interaction is strong.

*Predissociation by vibration:* In this case, a discrete vibrational level is coupled with a dissociative continuum of another vibrational mode within the same electronic state.

*Predissociation by rotation:* This kind of predissociation is caused by coupling between higher rotational levels of a discrete vibrational level with a dissociative continuum belonging to the same electronic state and vibrational mode.

Aryl halides generally dissociates via a predissociative mechanism when absorbing low energy photons (<5 eV). Systems that have been observed to exhibit this type of dissociation mechanism include C₆H₅I, C₆H₅Br, C₆H₅Cl. Here, predissociation is accomplished by electronic interaction, i.e. spin-orbit coupling between the initially excited singlet state and a repulsive triplet state.

![Fig. 5.2 An illustration of a predissociative mechanism. The initially excited electronic state is bound, but dissociates due to interaction with a repulsive state.](image)
5.3 Vibrational Dissociation

Vibrational dissociation occurs when enough energy is put into one specific vibrational mode to overcome the bond energy. The high vibrational levels of a given electronic state can be excited either directly with light or through internal conversion from a higher electronic state. In the latter case, dissociation is generally slow since internal conversion is a slow process. This type of dissociation is characterized in PTS experiments by a small fraction of translational energy and a low anisotropy. Moreover, if IVR is faster than the dissociation, the vibrational energy will be statistically distributed among the vibrational modes of the molecule and the rate of the dissociation can be predicted using statistical theories. Also, in this case the translational energy of the photofragments can be fitted with a Maxwell-Boltzmann distribution.

Dissociation via high vibrational levels of the electronic ground state has been suggested as a possible dissociation mechanism in for example chlorobenzene following excitation at 248 and 193 nm\(^2\).

Fig. 5.3 A schematic picture of a vibrational dissociation.
6 Photodissociation Dynamics of Aryl Halides

The main theme in this thesis is the ultrafast photodissociation dynamics of aryl halides, which was studied using femtosecond pump-probe spectroscopy. To begin with, the photodissociation dynamics of monohalogenated aryl halides (iodo-, bromo- and chlorobenzene) in the gas phase was investigated. Following these experiments we focused on the predissociation dynamics of bromobenzene. For this system we have studied the effect of halogen substitution (F, Cl and Br) and methyl group substitution at different positions on the phenyl ring. Also, as a guidance to interpret the results the potential energy surfaces were calculated for bromobenzene, o-, m- and p-dibromobenzene and 1,3,5-tribromobenzene. In addition to the molecular beam experiments, femtosecond transient absorption measurements were performed on bromobenzene in the condensed phase.

These experiments are presented in the following chapter. In the first section the pump-probe excitation scheme for the studied aryl halides is discussed.

6.1 The Pump-Probe Excitation Scheme of Aryl Halides

In the MB experiments the photodissociation dynamics of the different aryl halides after excitation with the pump pulse (266/270 nm) were measured by ionization of the excited molecules with the probe light (540 nm). Absorption of one pump photon promotes the molecules to an excited electronic state, which is ionized by

\[ \text{In experiments on bromobenzene, the probe wavelength has been varied between 535-570 nm to verify that the measured dynamics is independent of the probing step.} \]
absorption of two probe photons, as visualized in Fig. 6.1. If more than two probe photons are absorbed from the excited state, molecular fragmentation will be induced. In Fig. 6 the ionization process responsible for the pump-probe signal is indicated with solid arrows. Direct ionization of the ground state molecules with the pump and probe pulses separately is also possible. However, at the low intensities employed in the pump-probe experiments these ionization pathways are not efficient and the pump-probe process is the main ionization pathway. Accordingly, as the time delay between the pump and probe pulses is changed, the measured ion signal will reflect the dissociation dynamics of the excited state.

Note that in the experiments on iodo-, bromo- and chlorobenzene the formation of phenyl ions occurs via the excited state, but not through direct photoionization of phenyl radicals produced in the dissociation process. Since the vertical ionization potential of the phenyl radical is 9.13 eV \(^{46}\) it requires absorption of at least four probe photons, which is not likely at the low intensities, employed here. Therefore, both the signal from the molecular ion and the phenyl ion reflects the dynamics of the excited state. The same arguments can be applied in the bromotoluene experiments, since the ionization potential of the toluene radical is not likely to be substantially different from the ionization potential of the phenyl radical \(^{47}\). However, in the

![Diagram](image.png)

Fig. 6.1 A schematic model for photodissociation/photoionization of the studied monohalogenated aryl halides. These molecules are promoted to their first excited singlet state (S\(_1\)) by absorption of one pump photon. The pump-probe process is indicated with the solid arrows, whereas the dashed arrows show the additional pathway for ion formation, i.e. multiphoton ionization within the pump pulse.

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dihalogenated aryl halides, the neutral halobenzene radical produced in the dissociation can be ionized and the measured kinetics of this ion species is therefore more complicated. Therefore we focused on measuring the molecular ion signal in these systems.

6.2 Iodo-, Bromo- and Chlorobenzene

The pump-probe experiments on iodo-, bromo- and chlorobenzene are presented in paper I. In these experiments both the formation of molecular ions, \( C_6H_5X^+ \), and phenyl ions, \( C_6H_5^+ \), as a function of the time delay between the pump and probe pulses were monitored. According to the discussion in chapter 6.1, both the \( C_6H_5X^+ \) and the \( C_6H_5^+ \) reflect the dynamics of the excited state. The experimental traces are shown in Fig. 6.2.1. In iodobenzene, the signal could be fitted with a double exponential decay with time constants \( \tau_1 = 700 \) fs and \( \tau_2 = 350 \) fs. The decay of the signal in bromobenzene was single exponential with a time constant \( \tau_1 = 28 \) ps. In chlorobenzene, the lifetime of the excited state was much longer, with a decay rate on the ns timescale. These results are summarized in Table 6.2.1.

In earlier investigations of the photodissociation dynamics of aryl halides it has been suggested that the initially excited state is a bound singlet state that is predissociative due to spin-orbit coupling with a repulsive triplet state \( ^2 \) 21. This has been confirmed in our \textit{ab initio} calculations of bromobenzene 48, which are presented below. According to these calculations, when a pump wavelength of 266 nm is used, the molecules are promoted to their first excited singlet state, \( S_1 \), which is predissociative due to spin-orbit interaction with a repulsive triplet state \( (T_3) \), see the PES in Fig. 6.2.2. This mechanism results in the dissociation pathway assigned the time constant \( \tau_1 \) in bromobenzene and iodobenzene. In chlorobenzene, the spin-orbit interaction is weaker resulting in a slower intersystem crossing to the \( T_3 \) state. Therefore other decay processes, for example dissociation via high vibrational levels following internal conversion to the ground electronic state, may compete with the \( T_3 \leftarrow S_1 \) predissociation. A slow dissociation in chlorobenzene following excitation at 266 nm has been observed previously using the PTS technique 23.
In iodobenzene, the repulsive triplet state can be directly excited with 266 nm, resulting in the faster dissociation channel. Both time constants observed here in iodobenzene were in excellent agreement with earlier experiments performed by the group of Zewail\textsuperscript{25}. 

Fig. 6.2.1 Femtosecond transients obtained by detecting the molecular cations, C\textsubscript{6}H\textsubscript{5}X\textsuperscript{+} (left column), and the phenyl cations, C\textsubscript{6}H\textsubscript{5}\textsuperscript{+} (right column), produced from the parent compounds C\textsubscript{6}H\textsubscript{5}X, where X = I, Br, Cl. The open circles represent the pump-probe signal and the thin solid line corresponds to the ion signal with only the pump present. The thick solid line represents the single- or bi-exponential fit convoluted with the Gaussian instrument response function. The insets show the same transients on a shorter time scale.
Table 6.2.1 The lifetime of the excited state following excitation at 266 nm in the monohalogenated aryl halides.

<table>
<thead>
<tr>
<th></th>
<th>$\tau_1$ (ps)</th>
<th>$\tau_2$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_6$H$_5$I</td>
<td>0.7</td>
<td>0.35</td>
</tr>
<tr>
<td>C$_6$H$_5$Br</td>
<td>28</td>
<td>-</td>
</tr>
<tr>
<td>C$_6$H$_5$Cl</td>
<td>~1000</td>
<td>-</td>
</tr>
</tbody>
</table>

6.2.1 Different excitation energies in bromobenzene

In recent experiments in our group the rate of the predissociation of the S$_1$ state in bromobenzene has been found to notably depend on the excitation wavelength$^{49}$, see Table 6.2.2. The fastest predissociation was observed following excitation at 265.7 nm. At this energy, excitation is to the region of the S$_1$ surface where the coupling to the repulsive triplet surface is the strongest. With lower pump energies, the molecules are promoted to levels below the coupling region and the predissociation is slower. When the excitation energy was decreased below the tabulated values, the energy was not sufficient to reach the S$_1$ state and the pump-probe signal disappeared.

<table>
<thead>
<tr>
<th>Excitation wavelength (nm)</th>
<th>$\tau$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>262.0</td>
<td>23.5 ± 0.6</td>
</tr>
<tr>
<td>265.5</td>
<td>20.7 ± 0.6</td>
</tr>
<tr>
<td>269.0</td>
<td>27.6 ± 0.4</td>
</tr>
<tr>
<td>271.0</td>
<td>37.8 ± 0.4</td>
</tr>
<tr>
<td>272.5</td>
<td>35.6 ± 0.4</td>
</tr>
</tbody>
</table>

Table 6.2.2 The lifetime of the S$_1$ state in bromobenzene following excitation at different wavelengths.
6.2.2 \textit{Ab initio} calculations

In order to model the photodissociation process in bromobenzene, the potential energy surfaces for the lower lying electronic states that are relevant to our experiments were calculated along the C-Br coordinate. These calculations are presented in paper II. The calculations were performed at the complete active space SCF (CASSCF) level of theory, followed by multi-state multi-reference 2\textsuperscript{nd} order perturbation theory treatment (MS-CASPT2). Relativistic effects were included in the calculations, but the spin-orbit coupling was ignored. In the optimization, the geometry of the phenyl ring was kept equal to the relaxed ground state geometry.

From the calculations it is clear that using an excitation wavelength of 266 nm, the molecules are promoted to the B\textsubscript{1} (\(\pi, \pi^*\)) state (S\textsubscript{1}) with only a small excess vibrational energy. As mentioned above, a repulsive B\textsubscript{2} (n, \(\sigma^*\)) triplet state (T\textsubscript{3}) was found to cross the S\textsubscript{1} state near the excitation region. In addition, two lower lying bound triplet states of A\textsubscript{1} symmetry (T\textsubscript{1} and T\textsubscript{2}) were found in the calculations. From the S\textsubscript{1} state intersystem crossing to the T\textsubscript{1}, T\textsubscript{2} and T\textsubscript{3} states is symmetry allowed. However, since the S\textsubscript{1} and T\textsubscript{3} states cross, intersystem crossing between these two states is most probable.

![Ab initio potential energy surfaces along the C-Br coordinate for the relevant electronic states in bromobenzene. The vertical arrow indicates the calculated S\textsubscript{1}\leftarrow S\textsubscript{0} excitation energy.](image)

Fig. 6.2.2 \textit{Ab initio} potential energy surfaces along the C-Br coordinate for the relevant electronic states in bromobenzene. The vertical arrow indicates the calculated S\textsubscript{1}\leftarrow S\textsubscript{0} excitation energy.
6.2.3 The photodissociation of bromobenzene in solution

In paper II, the photodissociation dynamics of bromobenzene in solution were investigated following excitation at 266 nm. Femtosecond pump-probe experiments were performed in acetonitrile, n-hexane, tetrachloromethane and dichloromethane. In acetonitrile a broad spectral range was used for probing (290-800 nm), whereas in the other solvents the dynamics were probed at 400 and 800 nm.

The kinetics was characterized by a pulse-limited rise followed by decay on the ps timescale and a long-lived contribution (constant up to 200 ps) at all the analyzing wavelengths. In Fig. 6.2.3 the kinetics at two different probe wavelengths are shown.

![Fig. 6.2.3 The transient absorption of bromobenzene following excitation at 266 nm in acetonitrile solution. The kinetics was measured at 320 nm (triangles) and 710 nm (circles).](image)

The fast rise was assigned to excited state absorption and the subsequent decay, which was 9 ps in acetonitrile and similar in the other solvents, was assigned to predissociation via the repulsive triplet state (T₃). The long-lived contribution was tentatively assigned to absorption from one of the lower bound triplet states. In the wavelength range 420-620 nm an additional component that rises and decays within a few ps could be observed. The origin of this feature is not clear and possible explanations are discussed in the paper.

From these transient absorption measurements it is clear that the predissociation of bromobenzene occurs faster in all the investigated
solvents than in the gas phase. This is hardly surprising, since the solvent can induce symmetry perturbations and thereby increase the rate of ISC. Moreover, as the same predissociation rate was observed for all the analyzing wavelengths vibrational relaxation in the $S_1$ state does not occur to a significant extent.

6.3 Substituent Effects on the Photodissociation of Bromobenzene

During the last few years an increasing interest has been given to the effect of substitution on the photodissociation dynamics of aryl halides. The dissociation dynamics are affected in several ways through inductive and conjugative effects of the substituents. Also, substitution by a heavy atom can substantially increase the spin-orbit interaction. The predissociation process in bromobenzene has a suitable timescale for femtosecond pump-probe spectroscopy and therefore we have chosen this system for studies of substituent effects on the photodissociation dynamics. The substituents investigated include bromine, fluorine, chlorine and a methyl group.

When the conjugated $\pi$-system of aryl halides is excited, the dissociation dynamics is determined by the rate of intersystem crossing (ISC) and internal conversion (IC). The rate of these processes are given by the Fermi golden rule:

$$k = \frac{2\pi}{\hbar} H_{nm}^2 \rho_{eff}$$  

Eq. 6.3.1

where $H_{nm}^2$ is the coupling matrix element and $\rho_{eff}$ is the density of coupled states. Substituents can affect the coupling between states either by changing $H_{nm}^2$ or $\rho_{eff}$ and thereby affect the rates of ISC and IC.

Since bromine is a heavy atom it is expected to increase the spin-orbit coupling. Of the halogens studied here, it has the highest polarizability and lowest electronegativity. Fluorine, on the other hand, is a much lighter atom and should not affect the spin-orbit coupling as much as bromine. Also, it has the lowest polarizability and the highest electronegativity. Moreover, the halogen atoms have free p-electrons
that can be donated to the ring and thereby extend the conjugated system. The p-orbitals of fluorine have better overlap with the \( \pi \)-orbitals of the phenyl ring than the bromine p-orbital, which is larger and further out from the nucleus \(^{51}\). The conjugative effect should therefore be more important in fluorine than in bromine. Chlorine represents an intermediate case of the factors mentioned here. The inductive and conjugative effects affect the energy of the states, i.e. the position of the potential energy surfaces, which can change the coupling matrix element, \( H_{nn}^2 \), in Eq. 6.3.1. An increased spin-orbit coupling will also increase the coupling matrix element.

Substitution by a methyl group is not likely to affect the spin-orbit interaction since it is not a heavy group. Also, it has no free electrons that can be donated to the ring. However, the methyl group introduces a new degree of freedom to the molecule – the methyl group internal rotation. The internal rotational levels can increase the density of coupled states, \( \rho_{\text{eff}} \), and thereby increase the interaction between the initial and final states as shown by Eq. 6.3.1.

In the following sections the results from our femtosecond pump-probe experiments on the substituent effects on the predissociation of bromobenzene are summarized.

6.3.1 o-, m- and p-bromotoluene

In paper III in this thesis the effect of methyl group substitution on the photodissociation dynamics of bromobenzene have been investigated in o-, m- and p-bromotoluene.

The absorption spectra of the bromotoluene isomers are very similar to the UV absorption spectrum of bromobenzene, see Fig. 6.3.1. Analogous to bromobenzene, when 270 nm is used for excitation the \( S_1 \) state corresponding to a \( \pi^* \leftarrow \pi \) transition in the phenyl ring is excited in the bromotoluene isomers\(^{48,52}\).

In bromobenzene the \( S_1 \) state is predissociative due to spin-orbit interaction with a repulsive triplet state, and the molecules dissociates in \~ 36 ps following excitation at 270 nm\(^{49}\). A similar predissociative mechanism was suggested for the bromotoluene isomers. From our experiments we have determined the lifetime of the \( S_1 \) state to 14, 21
and 19 ps for o-, m- and p-bromotoluene, respectively. These experimental results are summarized in Table 6.3.1. The signal from both the molecular ion and the toluene ion was measured, and in agreement with the discussion in chapter 6.1, the signal from both ion species reflects the dynamics of the S₁ state.

The effect of methyl group substitution has been studied earlier for aryl halides. In o-, m- and p-bromotoluene the photodissociation dynamics following excitation at 266 nm was previously studied with the PTS technique⁵²,⁵³,⁵⁴. From these experiments it was deduced that

<table>
<thead>
<tr>
<th></th>
<th>τ (ps) molecular ion</th>
<th>τ (ps) toluene ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-CH₃-C₆H₄-Br</td>
<td>14 ± 1</td>
<td>14 ± 5</td>
</tr>
<tr>
<td>m-CH₃-C₆H₄-Br</td>
<td>21 ± 1</td>
<td>18 ± 5</td>
</tr>
<tr>
<td>p-CH₃-C₆H₄-Br</td>
<td>19 ± 1</td>
<td>19 ± 1</td>
</tr>
<tr>
<td>C₆H₅-Br</td>
<td>36 ± 1</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 6.3.1 The time constants for dissociation following excitation at 270 nm for the bromotoluene isomers and bromobenzene. The reason for the larger uncertainty in the toluene ion signal is that fewer measurements were performed on this species.
o- and m-bromotoluene dissociates via two different pathways, whereas the dissociation of p-bromotoluene occurs via only one channel. The dissociation pathway common for all the isomers was suggested to be the predissociative mechanism discussed above and the channel observed only in the o- and m-isomers was ascribed to dissociation via the high vibrational levels of the ground electronic state (hot molecule mechanism).

In other experiments it has been observed that the rate of IVR was substantially increased upon substituting one of the fluorine atoms in p-difluorobenzene for a methyl group\(^{55, 56, 57}\). The increased rate of IVR was attributed to an improved coupling between the vibrational states in the phenyl ring due to the rotational levels of the methyl group, which increases the effective coupled state density. Moreover, an increased probability for intersystem crossing was observed upon methyl group substitution in o-, m- and p-chlorotoluene in PTS experiments by Ichimura et al\(^{58}\). This observation was also explained by an increased coupled state density. Accordingly, the increase in the dissociation rate of bromotoluene as compared to bromobenzene observed in our experiments was attributed to an increased density of coupled states. The faster decay of the S\(_1\) state in o-bromotoluene than in m- and p-bromotoluene was ascribed to an even higher density of coupled states due to an almost free rotation of the methyl group\(^{59, 60, 61}\), which leads to a closer spacing of the rotational levels.

6.3.2 o-, m- and p-dibromobenzene and 1,3,5-tribromobenzene

In paper IV in this thesis, the photodissociation dynamics of o-, m- and p-dibromobenzene and 1,3,5-tribromobenzene were studied following excitation at 270 nm (4.6 eV) in the gas phase. As a guidance to further elucidate the dissociation processes of these compounds we have used quantum mechanical calculations. The potential energy surfaces along the dissociative C-Br coordinate of the ground state and several excited singlet and triplet states were calculated at the complete active space SCF (CASSCF) level of theory followed by multi-reference 2\(^{nd}\) order perturbation theory (CASPT2). All the calculations were performed with the MOLCAS program package. These calculations are presented in paper V in this thesis.
In Fig. 6.3.2 the kinetic transients of the molecular ions, C₆H₄Br₂⁺ from dibromobenzene and C₆H₃Br₃⁺ from 1,3,5-tribromobenzene, as a function of the time delay between the pump and the probe pulses are shown. The pump-probe signal in o- and m-dibromobenzene was fitted with double-exponential decays with time constants τ₁ and τ₂, whereas only one time constant, τ₁, was required to fit the signal from p-dibromobenzene and 1,3,5-tribromobenzene. The fitting results are summarized in Table 6.3.2. As the experiments were performed under magic angle conditions, the double-exponential decays in o- and m-dibromobenzene indicate that two different states were initially excited.

Excitation of the S₁ state is symmetry allowed in all the dibromobenzene isomers, but in 1,3,5-tribromobenzene, which belongs to the D₃h symmetry point group, it is forbidden. However, any vibration will reduce the symmetry and make a transition to the S₁ state allowed. As can be seen in the potential energy surfaces (presented in paper V) of these compounds, the S₁ state are crossed with a repulsive triplet state close to the excitation region. Intersystem crossing from S₁ to the triplet state is symmetry allowed in all the systems. Hence, in agreement with the photodissociation of bromobenzene, we have assigned the dissociation channel with time constant τ₁ to predissociation from the initially excited singlet state (S₁) via the repulsive triplet state. As τ₁ decreases with increasing number of bromine atoms it is consistent with a predissociative mechanism involving intersystem crossing. In addition, the lifetime of the excited state decreases with decreasing distance between the bromine atoms in the dibromobenzene isomers. As the contribution from the bromine substituent to spin-orbit interaction in the C-Br bond is determined by the amplitude with which its orbitals mix into the orbitals in the C-Br bond, which decrease rapidly with distance, this observation also supports the assignment. Note however, that the crossing point between the S₁ state and the repulsive triplet state is located at different energies in the different systems, which can also affect the dissociation rate.
Fig. 6.3.2. The yield of molecular cations, \( \text{C}_6\text{H}_4\text{Br}_2^+ \) from dibromobenzene and \( \text{C}_6\text{H}_3\text{Br}_3^+ \) from 1,3,5-tribromobenzene. In these traces, the constant ion signal from only the pump pulse has been subtracted.

The second, faster dissociation channel, assigned \( \tau_2 \) in table 6.3.2, observed in only o- and m-dibromobenzene has to originate from another state than \( S_1 \) as discussed above. Inspection of the potential energy surfaces shows that there are no other singlet states that can be excited at the excitation wavelength used, so the faster dissociation channel has to originate from excitation of a triplet state.

The transition probability, \( P \), to a triplet state can be estimated from Eq. 6.3.263.

\[
P \approx \left| \frac{\langle S_p \mid H^{30} \mid T \rangle}{E(S_p) - E(T)} \right|^2 \langle S_p \mid \rho_r \mid S_0 \rangle^2 \quad \text{Eq. 6.3.2}
\]

Hence, if excitation of a triplet state is to be allowed, the triplet state has to be mixed with a nearby singlet state, \( S_p \), and excitation of the \( S_p \) state from \( S_0 \) has to be symmetry allowed. Also, according to this
relation, the closer the $S_p$ and $T$ states are in energy, the stronger the transition intensity to the $T$ state.

In the energy region of the pump pulse (4.6 eV) the only singlet state is the $S_1$ state. $S_1$ is therefore the only state that can give transition intensity to a triplet state, i.e. $S_1$ is the $S_p$ state. For bromobenzene and all the dibromobenzene isomers, excitation of the $S_1$ state is symmetry allowed and the second factor in Eq. 6.3.2 is non-zero. Then, by evaluating the first factor in Eq. 6.3.2 it is clear that in o- and m-dibromobenzene the bound $T_3$ state is most likely excited. Lowering the point group symmetry makes internal conversion from $T_3$ to the $T_2$ state allowed\(^4\). As the potential barrier for dissociation in the $T_2$ state is low, lower than the crossing point between the $S_1$ state and the repulsive triplet state, this state is dissociative at the excitation energy used. This is a probable mechanism resulting in the second, faster dissociation channel assigned time constant $\tau_2$. Also, as the barrier in o-dibromobenzene is lower than in m-dibromobenzene, it agrees with the observation that $\tau_2$ was lower for o-dibromobenzene.

In p-dibromobenzene and bromobenzene the $T_2$ state should be excited according to Eq. 6.3.2. However, in these systems the potential barrier for C-Br bond breaking in $T_2$ is higher than the crossing point between the $S_1$ state and the repulsive $T_5$ state. Accordingly, molecules promoted to the $T_2$ state will not dissociate. Moreover, in p-dibromobenzene internal conversion from $T_2$ to $T_3$, which has a lower potential barrier, is forbidden. Hence, a process similar to the fast dissociation in o- and m-dibromobenzene is not possible.

For 1,3,5-tribromobenzene, which belongs to the $D_{3h}$ point group, only excitation of the $S_3$ state is allowed. According to Eq. 6.3.2, $S_3$ is the only state that can give transition intensity to a triplet state ($S_3$ is $S_p$). Keeping the $D_{3h}$ symmetry the first factor in Eq. 6.3.2 is only non-zero for the $T_4$ state, which is a bound state. Internal conversion to any other lower lying triplet state is symmetry forbidden, so a process similar to the fast dissociation in o- and m-dibromobenzene cannot occur. However, predissociation of the $T_4$ state due to intersystem

\(^4\) The point group symmetry of o- and m-dibromobenzene is $C_{2v}$. In the dissociation, the symmetry of these isomers is reduced to $C_s$. For p-dibromobenzene the point group symmetry is reduced from $D_{2h}$ to $C_{2v}$, while the $C_{2v}$ symmetry is preserved during the bond breaking in bromobenzene. The symmetry of 1,3,5-tribromobenzene is reduced from $D_{3h}$ to $C_{2v}$. 

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crossing to the repulsive singlet S₃ state is allowed, but as the vertical excitation energy of the S₃ state is higher than the excitation energy, the transition probability to the T₄ state is probably low. Therefore, this latter mechanism is not likely to occur.

6.3.3  o-, m- and p-bromofluorobenzene and o-, m- and p-
bromochlorobenzene

In very recent experiments, which are not yet published, we have investigated the photodissociation dynamics of o-, m- and p-
bromofluorobenzene and o-, m- and p-bromochlorobenzene following excitation at 270 nm.

Similar to the photodissociation dynamics of dibromobenzene at the same excitation energy, the o- and m-isomers of bromofluorobenzene and bromochlorobenzene showed double exponential decays (time constants τ₁ and τ₂), whereas the decay in the p-isomers was single exponential. The fitting parameters are listed in Table 6.3.2. Also here we have interpreted the dissociation process with time constant τ₁ as being due to predissociation of S₁ via a repulsive triplet state.

With fluorine substitution, the longest lifetime of the S₁ state was observed for the m-isomer, which dissociates with the same rate as bromobenzene. The S₁ state in the o- and p-isomers was observed to have the same lifetime, which was substantially shorter than the lifetime of the S₁ state in bromobenzene. As the rate of the dissociation does not increase with decreasing distance between the halogen atoms, as observed for the dibromobenzene system, the dominating effect of fluorine substitution is not an increased spin-orbit interaction. The fact that the m-isomer differs from the o- and p-isomers indicates that the conjugation effect is important, since it gives a lower electron density in m-position than in o- and p-position, which affects the potential energy surface

m- and p-bromofluorobenzene has previously been investigated with the PTS technique. In these experiments it was found that the fraction of available energy partitioned into translational energy was smaller for the p-isomer than the m-isomer. The fraction of translational energy was the same in m-bromofluorobenzene and bromobenzene. These results agree with our observations; the faster
the dissociation, the more of the available energy is partitioned into translation of the photofragments.

With chlorine substitution, the longest lifetime was also observed for the m-isomer. However in this case, the dissociation is significantly faster in the o-isomer than in the p-isomer. Hence, in these systems both spin-orbit interaction and the conjugation effect is important, which agrees with the fact that the mass of chlorine is in between the mass of fluorine and bromine. The electronic properties of chlorine are also in between the electronic properties of fluorine and bromine. The origin of the faster dissociation process in these systems is at the moment not completely understood. However, we tentatively assign the fast process to the same mechanism as in o- and m-dibromobenzene, i.e. excitation to a triplet state and subsequent internal conversion to another triplet state with a low barrier for dissociation.

<table>
<thead>
<tr>
<th></th>
<th>$A_1$</th>
<th>$\tau_1$/ps</th>
<th>$A_2$</th>
<th>$\tau_2$/ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br-C$_6$H$_5$</td>
<td>1</td>
<td>36 ± 1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>o-C$_6$H$_4$BrF</td>
<td>0.5</td>
<td>20.2 ± 0.3</td>
<td>0.5</td>
<td>4.4 ± 0.1</td>
</tr>
<tr>
<td>m-C$_6$H$_4$BrF</td>
<td>0.7</td>
<td>35.5 ± 0.5</td>
<td>0.3</td>
<td>9.0 ± 0.5</td>
</tr>
<tr>
<td>p-C$_6$H$_4$BrF</td>
<td>1</td>
<td>20.6 ± 0.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>o-C$_6$H$_4$BrCl</td>
<td>0.8</td>
<td>11.0 ± 0.6</td>
<td>0.2</td>
<td>1.2 ± 1.3</td>
</tr>
<tr>
<td>m-C$_6$H$_4$BrCl</td>
<td>0.9</td>
<td>27.2 ± 0.5</td>
<td>0.1</td>
<td>4.8 ± 1.1</td>
</tr>
<tr>
<td>p-C$_6$H$_4$BrCl</td>
<td>1.0</td>
<td>23.6 ± 0.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>o-C$_6$H$_4$Br$_2$</td>
<td>0.3</td>
<td>7.5 ± 1</td>
<td>0.7</td>
<td>1 ± 0.2</td>
</tr>
<tr>
<td>m-C$_6$H$_4$Br$_2$</td>
<td>0.6</td>
<td>13.3 ± 0.6</td>
<td>0.4</td>
<td>2.9 ± 0.4</td>
</tr>
<tr>
<td>p-C$_6$H$_4$Br$_2$</td>
<td>1</td>
<td>18.2 ± 0.2</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 6.3.2 The dissociation time constants and relative amplitudes of the studied aryl halides following excitation at 270 nm. The amplitudes ($A_1$, $A_2$) are normalized to one.
When diiodomethane, CH\textsubscript{2}I\textsubscript{2}, is dissociated with low energy photons (< 5 eV) it is known to form the CH\textsubscript{2}I radical and an I atom. The high anisotropy of the photofragments observed in PTS experiments led to the conclusion that the dissociation has to occur on a repulsive potential energy surface, i.e. the dissociation is direct. Also, the CH\textsubscript{2}I radical was found to be internally excited; about 80-90\% of the available energy appeared as rovibrational excitation.\textsuperscript{65, 66, 67} Moreover, in femtosecond pump-probe experiments in our group, a very fast dissociation of CH\textsubscript{2}I\textsubscript{2} was observed following excitation at 266 nm in the gas phase. The rate of the dissociation was found to be too high to be resolved from the cross-correlation (FWHM = 215 fs) of the pump and the probe pulse.

The photodissociation of CH\textsubscript{2}I\textsubscript{2} has also been studied in the condensed phase. However, the interpretations of these results are not as straightforward as in the gas phase experiments. Upon \(\gamma\)-radiolysis and UV-irradiation in the condensed phase a product with a strong absorption band centered at 380 nm and a weak absorption band around 570 nm has been observed. The origin of these absorption bands has been assigned to trapped electrons,\textsuperscript{68} the radical cation CH\textsubscript{2}I\textsubscript{2}\textsuperscript{+},\textsuperscript{69, 70, 71} and the isomer CH\textsubscript{2}I-I.\textsuperscript{72, 73}

In addition, the ultrafast dissociation dynamics of CH\textsubscript{2}I\textsubscript{2} in solution have been studied by several groups. The observed kinetic features are similar in the different experiments, although the interpretation of the results differs. In the first two studies it was concluded that the dissociation of CH\textsubscript{2}I\textsubscript{2} was completed faster than 100 fs.\textsuperscript{74, 75} The longer time dynamics were believed to originate from the CH\textsubscript{2}I radical and the radical cation CH\textsubscript{2}I\textsubscript{2}\textsuperscript{+}. In the latest femtosecond pump-probe experiment, the photodissociation dynamics of diiodomethane in acetonitrile solution was probed in a broad spectral range to give a more complete picture of the dynamics. From these experiments it
was concluded that the dissociation was somewhat slower than earlier suggested. The product absorption 50 ps after excitation was characterized by two bands; one strong centered around 390 nm and one weak around 560 nm, similar to the product absorption observed in the experiments discussed above. The isomer, CH$_2$I-I formed due to in-cage recombination of the photofragments was suggested to be responsible for these absorption bands. The timescale of formation of CH$_2$I-I was 1 ps$^{32}$.

Moreover, in resonance Raman experiments by the group of Phillips the photoproduct responsible for the strong absorption band around 385 nm observed on the ps and ns timescale has been identified as the CH$_2$I-I isomer by comparison with density functional theory calculations$^{76, 77}$. In other resonance Raman experiments the weak band centered on 570 nm was assigned to originate from both the CH$_2$I-I isomer and the radical cation CH$_2$I$_2^+$.$^{78}$

Hence, despite the numerous experiments the dissociation dynamics of CH$_2$I$_2$ in the condensed phase is not yet completely understood. The origin of certain kinetic features and absorption bands still needs to be elucidated. Therefore we have undertaken ab initio molecular dynamics simulations of the photodissociation of CH$_2$I$_2$ in acetonitrile solution, with the aim to study the cage effect.

7.1 The Photodissociation of Diiodomethane Studied with Ab Initio Molecular Dynamics Simulations

The photodissociation dynamics of diiodomethane in acetonitrile solution was studied using ab initio molecular dynamics simulations. The simulations were performed at room temperature in a cubic box using periodic boundary conditions. In the simulation box one diiodomethane molecule was surrounded by 31 acetonitrile molecules. The Car-Parrinello molecular dynamics (CPMD) program was used in the simulations.$^{79, 80}$

In the simulations, the system was equilibrated for 1 ps at room temperature in the electronic ground state. Thereafter the excitation was performed “by hand” by changing the description of the system. After excitation the system was described with the restricted open-shell Kohn-Sham method (ROKS)$^{81}$. The Car-Parrinello dynamics
was then followed on the excited state surface until the first encounter of the two iodine atoms. The system was then quenched back to the ground state.

In order to evaluate the solvent effect on the dissociation dynamics, the same simulations were also performed on an isolated molecule. The results from the simulations are shown in Fig. 7.1. Two different simulations were performed, one where the system was excited when the iodine atoms were at minimum distance, denoted exc-traj I, and one trajectory when the excitation was performed at a maximum distance, denoted exc-traj II. In both cases, a rapid dissociation of one of the C-I bonds could be observed. The remaining C-I bond gained a large amount of vibrational energy when the geometry was changed to the flat relaxed geometry of the CH₂I radical. The presence of the solvent damped this vibrational excitation to 50% within 500 fs. In exc-traj II the cage effect is clearly seen; in the gas phase simulation there is a fast separation of the photofragments whereas in the solution phase the photofragments are kept in the proximity of each other. Also, by comparing the gas phase trajectories with the solution phase trajectories it is visible that the solvent can influence which of the C-I bonds that is broken.

Upon quenching back to the ground state, the CH₂I-I isomer was immediately created. The trajectories after quenching are shown in Fig. 7.1.2. The I-I bond was formed vibrationally excited and also the C-H stretching and bending vibrations received a considerable amount of excitation. However, no vibrational excitation of the intact C-I bond could be observed.

To sum up, we have observed a prompt dissociation of diiodomethane; it occurs within 100 fs, which is in agreement with experimental findings. In the solution phase the solvent can influence which of the C-I bonds that is broken, which has been observed earlier in Raman experiments by the group of Phillips. Moreover, we have shown how the cage effect can lead to the formation of the diiodomethane isomer after photodissociation in acetonitrile solution. Upon isomer formation a strong vibrational excitation of the CH₂ modes was observed, which can be a characteristic feature of the intermediate CH₂I-I molecule. This vibrational excitation can possibly be used to experimentally confirm the suggested dynamical picture.
Fig. 7.1 The results from the gas phase simulations (thin lines) and the solution phase simulations (thick lines). The excitation was performed at time zero. In exc-traj II the system was excited when the I-I distance was at maximum and in exc-traj I at minimum. The solid and long-dashed lines correspond to the two C-I bonds and the short-dashed line shows the I-I bond. The C-H bonds are shown in a different timescale at the bottom of each graph.
8 Vibrational Wavepacket Dynamics

With the use of current femtosecond light sources coherent superpositions of vibrational eigenstates, vibrational wavepackets, can be created. In the simplest molecular system, the diatomic molecule, a vibrational wavepacket corresponds to the uncertainty in internuclear distance. The dynamics of the wavepacket thus represents the vibrational motion of the molecule or, if the state is dissociative, the breaking of the bond. Consequently, from studies of vibrational wavepackets we can learn about how chemical reactions proceed and even how to steer and control the outcome of a reaction. This field is currently of great interest and is often referred to as coherent control.

In order to study vibrational wavepackets certain requirements have to be fulfilled by the experimental technique. These are all realized by the pump-probe experiment. First, the pump pulse defines the time zero of the experiment. If the pump pulse is short enough in time a well-localized wavepacket can be created on the excited state potential energy surface. In a collision-free environment, such as in a molecular beam, the coherence of the molecules will be conserved and the observed motion can be considered as a single molecule trajectory.

Next, to be able to follow the vibrational motion a detection scheme that reflects the wavepacket dynamics has to be accomplished, i.e. it has to be molecular configuration sensitive. Different detection schemes that have been applied to probe vibrational wavepackets include laser induced fluorescence (LIF) and multiphoton ionization (MPI) followed by ion detection. With MPI, when the vibrational motion of lower excited electronic states is studied, higher excited electronic states can act as Franck-Condon windows. This leads to a higher ionization probability at certain internuclear distances and therefore a variation in ion signal as the bond length is changed in the vibrational motion. However, in studies of the vibrational dynamics in higher lying electronic states, one photon is sometimes sufficient to bring the molecule above the ionization threshold. As ionization
probability is usually assumed to be constant with internuclear separation\textsuperscript{83, 84}, the molecular configuration sensitivity of the probe process may be lost.

The main object of our investigation of vibrational wavepacket dynamics in the C ($^1\Sigma^+$) state in NaK was to elucidate the possibility of probing molecular wavepackets using single photon ionization. These studies are presented in the following section.

8.1 Vibrational Wavepacket Dynamics in NaK ($^1\Sigma^+$)

In paper VII a one-colour pump-probe setup has been used to investigate vibrational wavepacket dynamics employing a direct ionization detection scheme. With one pump photon at 529 nm the C ($^1\Sigma^+$) electronic state in NaK is excited. Absorption of one probe photon is then sufficient to promote the excited molecules to the ionic ground state, as is schematically shown in Fig. 8.1.1. The experimental trace is shown in Fig. 8.1.2a. Although one usually assumes that the ionization probability is constant with internuclear separation as mentioned above, a modulation with a period of 500 fs in the ion yield was clearly seen in the experimental trace. The oscillation was in phase with the peak at time zero, implying that there is an enhanced ionization probability at the position where the wavepacket is created. This is visualized in Fig. 8.1.1; the wavepacket is created on the inner turning point of the C potential energy surfaces and also ionized at the same position. Fig. 8.1.2.b shows the results from classical r-centroid calculations, which yields an oscillation period of 510 fs.

In order to gain further insight into the factors that governs direct ionization of the vibrational wavepacket we have derived a simple analytical expression describing the ionization step:

\[
P_i(\omega_{pu}, \omega_{pr}, \tau) \propto \frac{1}{2} \left( 1 + \text{erf} \left( \frac{\sqrt{2}}{\alpha} (\omega_{pu} - D(r_i)) \right) \right)
\]

Eq. 8.1
Fig. 8.1.1 A schematic illustration of the one-colour pump-probe scheme and the potential energy surfaces of interest for the experiment. Absorption of one pump photon (529 nm) brings the molecules to the C state, which is subsequently ionized by absorption of one probe photon.

In the derivation of Eq. 8.1, we have applied the short time approximation and also assumed that the difference potential for the ionization step, \( D(r) = V_i(r) - V_i(r) \), varies slowly over the wavepacket width. Also, the transition dipole moment, \( \mu \), is assumed to be constant with \( r \) and \( E \). The probe pulse is described with a Gaussian function, where \( \alpha \) is the width. For short times the wavepacket is well localized and the wavepacket trajectory, \( r_\tau \), can be followed by solving the classical Hamilton equations of motion. Then, using Eq. 8.1 to calculate the ion signal yields an oscillatory motion with a period of 495 fs, which is in excellent agreement with the experimentally observed period (500 fs) and the classical r-centroid calculations (510 fs). Also the phase of the oscillation agrees with the

\[ \omega_{pr} \]

\[ \omega_{pu} \]

\[ C^1\Sigma^+ \]

\[ X^1\Sigma^+ \]

\[ X^2\Sigma^+ \]

3 Using Eq. 8.1 to simulate the ion signal neglects temperature effects. In the r-centroid calculations the effect of a finite temperature of the molecules was included by assuming a Boltzmann distribution in the electronic ground state.
Fig. 8.1.2. The yield of NaK$^+$ as a function of time delay between the pump and probe pulses a) experimental trace b) the theoretical results obtained from the classical $r$-centroid calculations.

experimentally observed. According to Eq. 8.1 a modulation of the ion yield is obtained if the energy of the probe pulse does not exceed the difference potential at all internuclear separations. However, the calculated amplitude of the oscillation is much smaller than what was observed in the experiment. We believe that this is due to a transition dipole moment that varies with internuclear separation, giving a higher ionization probability at the inner turning point of the C potential energy surface. The calculated results from Eq. 8.1 can together with the experimental results be used to predict the variation of $\mu$ as $\mu(r) \sim \mu_0(1-0.1r)$. Hence, our measurement is consistent with a photoionization transition dipole moment of the C ($^1\Sigma^+$) that varies with internuclear separation.
9 Summary

Using femtosecond pump-probe spectroscopy we have observed how the rate of dissociation of the monohalogenated aryl halides, iodo-, bromo- and chlorobenzene, in the gas phase following excitation at 266 nm increased with increasing mass of the halogen atom. The dissociation mechanism was assigned to predissociation of the initially excited singlet ($\pi, \pi^*$) state via a repulsive triplet ($\pi, \sigma^*$) state. In iodobenzene a direct dissociation channel was also observed. The suggested dissociation mechanism has been confirmed in \textit{ab initio} calculations of the potential energy surfaces of the ground state and several low lying excited states in bromobenzene. A solvent environment was observed to increase the rate of the predissociation in bromobenzene. This observation was attributed to solvent-induced symmetry perturbations. The predissociation rate of bromobenzene was also affected by substituting one of the hydrogen atoms. In o-, m- and p-dibromobenzene the predissociation rate increased with decreasing distance between the bromine atoms in accordance with an increased spin-orbit interaction introduced by the bromine substituent. With chlorine and fluorine substitution, inductive and conjugative effects were found to be important. In addition to the predissociation channel, a second faster dissociation pathway was observed in the o- and m-isomers of the dihalogenated aryl halides. Using \textit{ab initio} calculations of the potential energy surfaces in the dibromobenzene isomers, we could assign the fast dissociation pathway to predissociation of an initially excited triplet state.

In Car-Parrinello molecular dynamics of diiodomethane in acetonitrile solution we have observed a direct dissociation occurring within 100 fs. The cage effect leads to formation of the isomer, CH$_2$I-I.

Vibrational wavepacket dynamics has been studied in the C ($^1\Sigma^+$) state of NaK in order to elucidate the possibility of probing wavepackets by single photon ionization. The photoionization transition dipole moment was found to vary with internuclear distance.
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