Exploring molecular dynamics for coherent control

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Chapter 1

Introduction

Since the early days of lasers, exploring and controlling basic chemical reactions has been considered as one of the most intriguing area of laser applications. The recent appearance of laser systems producing femtosecond pulses has opened a new field of physical chemistry, the so called femtochemistry [1]. Pump-probe measurements in the femtosecond time domain become a powerful tool to investigate different aspects of molecular dynamics, like dissociation, internal vibrational energy redistribution or isomerization [2, 3, 4, 5]. With the help of a cleverly shaped laser pulse or a properly chosen sequence of pulses a real-time control of molecular dynamics has also become possible [6]. In this way molecules can be forced to follow reaction pathways which, without an external field, are either energetically forbidden or simply too inefficient or could not even be activated by conventional methods. [6, 7, 8]. Problems like controlling product ratio [9], breaking the stronger bond rather than the weaker one [10], controlling vibrational motion [11, 12], isomerization [13] have been addressed. As a solution different control scenarios using ultrashort laser pulses have been developed. According to the approach, proposed by Judson and Rabitz, [14] the control pulse is optimized iteratively in a closed loop with the help of self-learning algorithms [15] using a feedback signal from the experiment. The advantage of this approach is that it requires in principle only minimal knowledge about the system. Its main goal is only to achieve the desired control, but an insight into the mechanism, with which the actual control is achieved is neither necessary beforehand nor can easily be gained from the optimized control pulse. Nevertheless extensive work have been in progress to support the experiments with control fields optimized in theory. [16, 17]

A different approach of control with femtosecond laser pulses based on an extensive knowledge about the molecule was proposed by Tannor and Rice [18]. In this control scheme the molecule is driven to an excited electronic state by the first laser pulse. As the wavepacket
of the nuclei propagates on the excited state potential surface it is intercepted by a second laser pulse which dumps the wavepacket back to the ground state such that finally the desired chemical state is achieved. Such two color control schemes offer great practical potential in controlling chemical reaction [12, 19, 20, 21]. Nevertheless, in order to plan a Tannor-Rice control scheme for a particular molecule or to understand the mechanism underlying the results of a pump-probe measurement, the quantum dynamics of the molecule should be followed [22]. A fundamental prerequisite for this is to establish the relevant potential energy surfaces either by constructing model potentials or computing them with quantum-chemical methods. (Other molecular properties, such as potential couplings and transition dipole moments should also be known beforehand.)

The present work consists of two distinct parts, both concerning some particular theoretical aspect of femtochemistry, mentioned above, namely i) exploring the dynamics underlying the results of a pump-probe experiment via wavepacket simulations, ii) \textit{ab initio} computing potential energy surfaces as well as transition dipole moments. The motivation of both parts is the same: to reveal the possibility of controlling molecular dissociation. In both parts the spatio-temporal evolution of populations in different electronic states induced by femtosecond laser pulses was followed by numerical simulations. Thus first in section 1.1 the common theoretical background of both parts will be presented. Then, as the first topic, simulations are performed in chapter 2 to give an explanation of the results obtained from the pump-probe experiment on CsCl, performed by A. Glaß [23, 24]. The understanding of these results served for theoretical basis of the subsequent optimal control of the dissociation of this molecule. [25] The main goal of this experiment was to demonstrate the power of controlling molecular reactions with femtosecond laser pulses in the strong response regime, i.e., with pulse intensities in the region of 1 TW/cm$^2$ which result in a strong population transfer to excited states.

In chapter 3, the photodissociation dynamics of the CH$_2$BrCl molecule is investigated as the second topic of the present work. The reason for investigating this molecule is that the photochemistry of halomethanes has received significant attention in the recent years. Besides their environmental importance$^1$, halomethanes have become a subject of fundamental investigations of photodissociation reactions. They have been chosen as pro-

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$^1$Halogen atoms are well known to contribute to ozone depletion in the stratosphere [26]. Especially bromine containing compounds have attracted an increasing interest in the atmospheric chemistry community [27, 28, 29, 30, 31, 32] due to the powerful ozon depletion potential of atomic bromine [33]. Additional interest on CH$_2$BrCl comes from its industrial applications as a possible replacement for CF$_3$Br and CF$_2$ClBr in some fire suppressants.
prototypes for mode specific photochemistry upon laser excitation, and therefore a lot of questions have been raised regarding the mechanism by which preferential dissociation takes place [10, 28, 32, 34, 35, 36, 37, 38, 39, 40, 41, 42]. For example the photodissociation of CH$_2$BrI was investigated thoroughly and a selective fragmentation of the stronger C-Br bond rather than the weaker C-I one was observed at 210 nm, on the contrary to excitations at 248 or 193 nm where both fissions were observed [35, 36]. Recently it has been theoretically shown that it is also possible to control this branching ratio by means of coherent control, i.e. using constructive or destructive interference of coherent absorption pathways [42]. In CH$_2$BrCl only femtosecond adaptive pulse shaping has recently succeeded in really controlling C-Cl versus C-Br cleavage [10]. However, this technique was used only to maximize or minimize the ion CH$_2$Br$^+$/CH$_2$Cl$^+$ ratio, which poses questions about whether the control is actually achieved in neutral or ionic surfaces.

The few models which have tried to understand the photodynamics in halomethanes indicated that the nonadiabatic curve crossing plays an important role in these species, [30, 31, 38, 39, 40]. Nevertheless, all available studies were based on simple model potentials for the n → σ$^*$ excited states in the C-X and C-Y reaction coordinates, coupled by some arbitrary strength [37, 39, 42] and therefore trends are difficult to generalize. Which pathway the system follows after a specific excitation is a question that has not yet been answered. The lack of accurate potential energy surfaces for halomethanes prevents one from reaching firm conclusions. Therefore in chapter 3 the emphasis was laid on computing the vertical spectra and the potential energy curves of CH$_2$BrCl. As an alternative to the control experiment reported in Ref. [10], a Tannor-Rice control scheme, similar to the one applied for the CsCl molecule by A. Glaß [23, 24, 25], is proposed, aiming the selective bond breakage in the neutral dissociation channel.
1.1 Theoretical background: general considerations

The dynamics of a molecule is governed by the time dependent Schrödinger equation (TDSE). In most cases, one is interested in the internal motion of the molecule, thus the TDSE is treated in the center of mass coordinate system, as will be the case throughout the present work as well, neglecting the translational motion of the molecule as a whole. In the case when no interaction with an external electric field is present, the TDSE can be written in the following form

\[
i\hbar \frac{\partial \chi(R, r, t)}{\partial t} = \hat{H}_{mol}(R, r) \chi(R, r, t) = (\hat{T}^{nu} + \hat{T}^{el} + \hat{U}(R, r)) \chi(R, r, t) , \tag{1.1}
\]

where \( \hat{H}_{mol}(R, r) \) is the total molecular Hamiltonian operator and \( \chi(R, r, t) \) is the total wavefunction of the molecule with \( R \) and \( r \) denoting the coordinates of all the nuclei and electrons, respectively. The operators \( \hat{T}^{nu} \) and \( \hat{T}^{el} \) stand for the kinetic energies of the nuclei and electrons, respectively, while the potential \( \hat{U}(R, r) \) contains the Coulomb energy terms

\[
\hat{U}(R, r) = \frac{1}{4\pi\epsilon_0} \left( \sum_i \sum_{j<i} \frac{e^2}{|r_i - r_j|} + \sum_I \sum_{J<I} \frac{Z_I Z_J e^2}{|R_I - R_J|} - \sum_i \frac{Z_I e^2}{|R_I - r_i|} \right) . \tag{1.2}
\]

The summations for \( i, j \) and \( I, J \) go over the electrons and nuclei, respectively. \( Z_I \) is the charge number of the nucleus, \( I \).

The first of several approximations used in the present work is the Born-Oppenheimer approximation. It assumes that the motion of the nuclei and that of the electrons can be separated due to the large difference between their masses. In other words, the electrons follow instantaneously the motion of the nuclei and thus always reside in some stationary state belonging to the actual coordinates of the nuclei. Hence, the solution of the TDSE may be written as an expansion of time-independent electronic functions

\[
\chi(R, r, t) = \sum_j \Psi_j(R, t) \Theta_j(R, r) , \tag{1.3}
\]

where the \( \Theta_j(R, r) \) form an orthonormal set of electronic wavefunctions (electronic states) and the time dependent coefficients, \( \Psi_j(R, t) \) are regarded as the wavefunctions describing the motion of the nuclei. That is, the \( |\Psi_j(R, t)|^2 \) represents the probability density, that at time \( t \) the molecule resides in the electronic state \( j \) with the nuclear coordinates \( R \). The total probability, \( P_j(t) \), of the molecule being in the \( j \)th electronic state at time \( t \), i.e., the population of the electronic state \( j \) at \( t \), is generally given by

\[
P_j(t) = \langle \Psi_j(R, t)|\Psi_j(R, t) \rangle . \tag{1.4}
\]
The time evolution of the populations \( P_j(t) \) are called the population dynamics. In the adiabatic representation the \( \Theta_j(R, r) \)'s are eigenfunctions of the electronic Hamiltonian operator, \( \hat{H}^e(R, r) = \hat{H}_{\text{mol}}(R, r) - \hat{T}^{\text{nu}} \) for each nuclear coordinate \( R \), i.e., they are the solutions of the time-independent Schrödinger equation (TISE)

\[
\hat{H}^e(R, r) \Theta_j^a(R, r) = \left( \hat{T}^{\text{el}} + \hat{U}(R, r) \right) \Theta_j^a(R, r) = \lambda_j^a \Theta_j^a(R, r) \quad (1.5)
\]

for the electron system. Here, the superscript \( a \) refers to the adiabatic representation. The eigenvalues, \( \lambda_j^a(R) \) form the adiabatic potential energy surfaces. An exact description of the system would require the set of \( \Theta_j(R, r) \) to be complete. In practice, however, only a finite set of electronic states is involved in the expansion in Eq. 1.3, namely those states (potentials) which play a non-negligible role in the process to be described.

Considering only one nuclear coordinate, \( Q \), the TDSE for the nuclear wavefunctions takes the form

\[
i\hbar \frac{\partial \Psi_j^a(Q, t)}{\partial t} = \sum_k \hat{H}_{jk}^{nu,a} \Psi_k^a(Q, t). \quad (1.6)
\]

where \( \hat{H}_{jk}^{nu,a} \) is the element of the nuclear Hamiltonian operator \( \hat{H}^{nu} \) in the adiabatic representation defined as

\[
\hat{H}_{jk}^{nu,a} = \delta_{jk} \left( \hat{T}^{\text{nu}} + V_j^a(Q) \right) - \frac{\hbar^2}{2m} \left( T_{jk}^{(2)} + 2T_{jk}^{(1)} \nabla Q \right), \quad (1.7)
\]

where \( T_{jk}^{(1)} \) and \( T_{jk}^{(2)} \) are defined as

\[
T_{jk}^{(1)}(Q) = \langle \Theta_j^a(Q, r) | \frac{\partial}{\partial Q} \Theta_k^a(Q, r) \rangle, \tag{1.8a}
\]

\[
T_{jk}^{(2)}(Q) = \langle \Theta_j^a(Q, r) | \frac{\partial^2}{\partial Q^2} \Theta_k^a(Q, r) \rangle. \tag{1.8b}
\]

Here, \( m \) is the reduced mass of the molecule corresponding to the one dimensional motion along internal coordinate, \( Q \) and the subscript \( r \) in \( \langle ... \rangle_r \) is used to emphasize that the integration is performed only over the electron coordinates, \( r \). The off-diagonal elements, \( T_{jk}^{(1)} \) and \( T_{jk}^{(2)} \) \( (j \neq k) \) are respectively the first- and second-order non-adiabatic kinetic coupling elements between the electronic states \( j \) and \( k \). The diagonal elements \( T_{jj}^{(1)} \) and \( T_{jj}^{(2)} \) together form the so-called diagonal correction to the adiabatic potentials, \( V_j^a(Q) \). It can be shown that this correction is smaller than \( V_j^a(Q) \) by a factor roughly equal to the ratio of the electronic and nuclear masses, thus in the BO-approximation this diagonal correction is neglected. On the other hand, in the adiabatic approximation all the kinetic
coupling elements are neglected. Applying both approximations, the TDSE reduces to the form

\[ i\hbar \frac{\partial \Psi_a^j(Q, t)}{\partial t} = (\hat{T}^{nu} + V_a^\alpha(Q))\Psi_a^j(Q, t) . \]  

This form of the TDSE can be used for simulating the molecular dynamics only in absence of any coupling between the adiabatic potentials. It is inadequate in the vicinity of avoided crossings where an intrinsic coupling between the potentials allow the molecule to go from one electronic state to the other. In this case, one needs to solve the original equation 1.6 or an equation physically equivalent to it (see later in section 3.2.2 the TDSE in the diabatic representation). The interaction with an external electric field may also establish a coupling between the electronic states, allowing the transfer between states of different energies.

In the present work the laser coupling was treated in the semiclassical dipole approximation\(^2\) so that the new Hamiltonian, \(\hat{H}\) is written as

\[ \hat{H}(Q, t) = \hat{H}^{nu}(Q) - \xi(t) \mu(Q) , \]  

where \(\xi(t)\) is the electric field of the laser and \(\mu\) is the electronic dipole moment (TDM) matrix. The off-diagonal terms of the TDM matrix are the transition dipole moment vectors. In case of each simulation in the present work, the diagonal elements of the TDM matrix (i.e. the dipole moments) were set to zero because they do not play a role considering transitions induced by UV or visible photons. The TDM matrix elements are defined as

\[ \mu_{jk}(Q) = e \langle \Theta_j(Q, r) | r | \Theta_k(Q, r) \rangle_r . \]  

Throughout the present work the TDSE was solved numerically using the split operator (SPO) method. [43, 44] The SPO method is based on the approximation, that choosing the time interval, \(dt\) sufficiently small, the Hamilton operator \(\hat{H}(Q, t)\) can be regarded as constant within \(dt\) and the change of the nuclear wavefunction, \(\Psi = [\Psi_1, \Psi_2, ...]\), during this time can be expressed in the form

\[ \Psi(Q, t + dt) = e^{-i\hat{H}(Q, t)dt/h}\Psi(Q, t) . \]  

Using the approximation

\[ e^{-i\hat{H}(Q, t)dt/h} \simeq e^{-i\hat{T}^{nu}dt/2h} e^{-i\hat{V}^\alpha(Q)dt/2h} e^{-i\xi(t)dt/h} e^{-i\hat{V}^\alpha(Q)dt/2h} e^{-i\hat{T}^{nu}dt/2h} \]

\[ (1.13) \]

\(^2\)The classical treatment of the electric field is possible because the number of photons in the laser pulse is sufficiently large. The dipole approximation reflects the fact, that the size of the molecules is negligible with respect to the wavelengths of the applied laser fields.
one has to compute subsequently the effects of the individual exponentials on the wavefunctions. Since $\hat{T}^{nu}$ is a multiplication in the momentum space, the corresponding exponential is evaluated by transforming the wavefunction from coordinate space to the momentum space using fast Fourier transformation (FFT) [45], multiplying by $\exp(-ik^2dt/2)$ (where $k$ is the wave number) and transforming back to the coordinate space. In case of the exponentials of non-diagonal parts of the Hamiltonian (e.g. non-adiabatic potential coupling or coupling with laser field, like in Eq. 1.13) the wavefunction should be back-and forth transformed into a proper adiabatic representation where the operators are diagonal.

For each of the quantum dynamical computations of the present work the same initial condition was used: it was assumed that the molecule initially resides in its electronic ground state in a vibrational eigenstate. Hence, as a first step the corresponding wavefunction has to be determined. Although there exist approximate analytical solutions for certain potential shapes, (e.g. for Morse-potentials), the eigenfunctions were in all cases computed numerically according to the Fourier Grid Hamiltonian (FGH) method. [46] This method uses the matrix-discretization of the Hamiltonian operator in the coordinate space. The element $l$ of the kinetic operator $\hat{T}^{nu}$ in the momentum grid representation can be written as

$$T_l = \frac{2}{m} \left( \frac{\hbar \pi l}{N \Delta x} \right)^2,$$  \hspace{1cm} (1.14)

where $N$ is the (odd) number of grid points in the spatial grid and $\Delta x$ is the spatial grid spacing. Let $\mathcal{F}$ denote the matrix, which represents the forward FFT and $\xi_n$ denote the $n$th eigenvector of the space operator $\hat{x}$ in the coordinate representation (i.e. the $\xi_n$ denote the column vector composed entirely of zeros except for a single element of unity in the $n$th row). Then the elements of the Hamiltonian matrix are constructed as

$$H_{in} = \left[ (\mathcal{F}^{-1}T\mathcal{F} + V ) \xi_n \right]_i,$$ \hspace{1cm} (1.15)

where $T$ and $V$ are the diagonal kinetic energy and potential energy ($V(x_i)$) matrices. The eigenvalues and the eigenfunctions of the $H_{in}$ matrix are directly the vibrational energies and the spatially discretized form of the eigenfunctions of the potential, represented by $V(x_i)$.

In Chapter 2 numerical simulations will be performed using model potential curves given by analytic expressions fitted to spectroscopic data. Transition dipole moments will also be estimated from measured absorption cross sections. Since in the experiments ionization
played a crucial role, an extension of equations 1.9 and 1.10 will be used to describe the ionization process, too. In Chapter 3 the emphasis will be laid on computing accurate \textit{ab initio} potentials for the quasi-triatomic CH$_2$BrCl molecule in order to model the non-adiabatic dissociation dynamics.
Chapter 2

Control of CsCl dissociation

2.1 Overview

The aim of the work discussed in the present chapter was to support the experiments performed by Glaß et.al. [23, 24, 25] with the help of numerical simulations. All the experimental data reported in the present chapter are adapted from the Ph.D. thesis of A. Glaß [24]. A detailed description of the experimental setup is given in Refs. [23, 24, 25].

The goal of the experiments was to control the photodissociation of the CsCl molecule according to the Tannor-Rice scheme [18]. The concept of the control is shown schematically in Fig 2.1 and can be understood as follows [47, 48]. At time $t_0$ the wavepacket resting in the CsCl ground state (state X in Fig. 2.2) is resonantly excited by a fs UV laser pulse to the first excited state (state A in Fig. 2.2). Due to the repulsive nature of the first excited state potential the wavepacket starts to move towards larger internuclear separations. The control task is to ”glue” the atoms of the dissociating molecule together optically with a second (control) pulse, i.e., to stop the ongoing dissociation by resonantly de-exciting the molecule to the ground state at time $t_1$ with the help of a fs VIS laser pulse. If the VIS pulse is applied at any other time only a small portion of the wavepacket will be transferred back to the ground state. Thus the time delay between the UV and the VIS pulses is the crucial parameter that determines the efficiency of the control process.

The laser pulses were produced by a XeCl-excimer laser pumped dye laser system [49], chirped in a polarization preserving fiber and compressed by a prism compressor [50] yielding a VIS pulses at 497 nm. These pulses were then frequency doubled and UV pulses at 248.5 nm were produced, which is almost exactly in resonance with the $X \rightarrow A$ transition energy for the ground state equilibrium internuclear distance. The width of
Figure 2.1: Application of the Tannor-Rice control scheme: At time $t_0$ the molecule is excited by a femtosecond pump pulse of wavelength $\lambda_1$ from ground state X to the excited state A. Since this state is repulsive, the molecule starts dissociating. The control pulse with a properly chosen wavelength, $\lambda_2$ at a properly chosen time, $t_1$ can resonantly depump the molecule to the ground electronic state, i.e., optically gluing the atoms together.

the pulses could be varied by changing the prism distance. The relative polarization of the UV and that of the VIS pulses was adjusted by a $\lambda/2$ plate inserted in the beam line of the VIS pulse. After introducing a variable delay between the fundamental and the second harmonic pulses both were focused collinearly into the CsCl molecular beam in a vacuum chamber. The focus diameter, $D$ was $(25 \pm 5) \mu m$ for the UV and $(40 \pm 5) \mu m$ for the VIS laser beam, respectively. These values correspond to maximum intensities, $I_0$ of $(0.8 \pm 0.3)$ TW/cm$^2$ at 100 fs pulse width (FWHM) for the UV and $(5.3 \pm 1.1)$ TW/cm$^2$ at the minimal pulse width of 50 fs for the VIS laser pulses. (Definitions of $I_0$ and $D$ are given in the next section.) As an experimental signal Cs$^+$ ions produced in the interaction region were detected with a quadrupole mass spectrometer. Considering the depumping and ionization by the second pulse as two competing processes, one would expect a dip in the ion-signal versus the delay time at the delay of $t_1-t_0$, optimal for the depumping. As will be seen, just the opposite was measured. Theoretical investigations by wavepacket propagation were then necessary to find an explanation. Results of these investigations together with the experimental results are discussed in this chapter. All the numerical simulations presented in this chapter were performed on an RS6000/F40 (Power PC604e,

\[1\] The polarization of the UV light coming out from the frequency doubling crystal was perpendicular to the polarization of the fundamental VIS light. However, assuming that both the X$\rightarrow$A in the FC-region and the A$\rightarrow$X at around 5.75Å are parallel transitions, the pump-dump scheme prefers a parallel polarization of the UV and VIS electric fields. The number of Cs$^+$ ions produced by the subsequent pulses was indeed found to be maximal for parallel polarization. Thus all the experimental results referred here were obtained using parallel polarized UV and VIS pulses.

\[2\] The actual pulse parameters used in the pump-probe measurements are slightly different from these values as indicated later.


Figure 2.2: The relevant electronic potential curves of CsCl are shown with the asymptotic atomic states of Cs and Cl including the corresponding asymptotic energies in parentheses. An intersection between the ground state and the first excited state occurs at 51 Å. The ionization continuum of Cs lies above 3.89 eV.

2.2 Theoretical model

In this section the theoretical model used for the simulations is described. The wavepacket dynamics was simulated by solving the time dependent Schrödinger equation numerically. Since the molecules in the experiment were prepared in a cold molecular beam, no thermal averaging over the initial states had to be performed so the initial wavefunction was chosen in the simulations always as the lowest vibrational eigenfunction of the ground electronic state potential, X. The interaction of the molecules with the radiation field was described in the dipole approximation using real electric fields. In all simulations the pulses were assumed to be Gaussian in time. Since data concerning the transition dipole moments were only available either for the CsCl molecule in its equilibrium geometry or for the isolated Cs atom, all the transition dipole moments were assumed to be independent of the internuclear distance. The ionization process was computed according to the method of discretizing the ionization continuum [51, 52]. The transition dipole moment distributions to the continuum were taken as positive constants within a range $[0, E_{max}]$ of the kinetic energy of the emitted photoelectrons. Otherwise they were supposed to be zero.

The electric field vector, $\varepsilon(t)$ for one laser-pulse can be written as

$$\varepsilon(t) = E(t) \cos(\omega t + \phi) ,$$

(2.1)
where $\omega$ is the instantaneous laser-frequency\(^3\), $\phi$ is a constant phase-factor (playing usually no role in the interaction between the molecules and the electric field). The first term, $E(t)$ on the right hand side of Eq. 2.1 is the envelope of the electric field, that varies slowly compared to the second term. Throughout the present work linearly polarized laser pulses will be considered and $\varepsilon(t)$ and $E(t)$ will denote the $|\varepsilon(t)|$ and $|E(t)|$, respectively. The intensity of the pulse is then given by

$$I(t) = \frac{1}{2} c n \epsilon_0 E^2(t)$$

(2.2)

where $c$ is the speed of the light, $n$ is the refractive index of the medium\(^4\) and $\epsilon_0$ is the vacuum-dielectric constant. A focused pulse with a Gaussian temporal and spatial beam-profile has the following spatiotemporal intensity distribution, $I(\rho, t)$ in the focal plane:

$$I(\rho, t) = I_0 \exp \left( -4 \frac{\rho^2}{D^2} \right) \exp \left( -4 \ln \frac{2(t - t_0)^2}{\tau^2} \right)$$

(2.3)

where $\rho$ is the radial distance from the beam-axis, $D$ is the focus diameter, $t_0$ is the time belonging to the center of the pulse and $\tau$ is the temporal width of the pulse, i.e., the full width at half maximum (FWHM). Throughout the present work the 'intensity' (or 'peak intensity') of a pulse will refer to $I_0$.

In order to compute correctly the one-pulse and the pump-probe signals, one should, in general, consider the intensity profile of the laser beams as well as the orientation-distribution of the molecules. In the dipole approximation for small intensities the probability of a one-photon transition (like the X$\rightarrow$A with the UV pulse) is determined by the vector product of the electric field vector and the transition dipole moment vector. More specifically it is proportional to $\cos^2 \beta$ where $\beta$ is the angle between the polarization of the electric field and the transition dipole moment vector. Since the orientation-distribution of the molecules is uniform before the interaction with the laser pulses, the pump-probe signal should have been computed for all possible $\beta$-s and then averaged with the appropriate distribution function. A similar averaging over the spatial intensity distribution should have also been performed.

These, however, would have increased the computational time enormously, so these averaging were not performed for the pump-probe simulations but their possible effects on the signals will be discussed later.

---

\(^3\)The instantaneous frequency, $\omega$ itself is usually also a function of the time and can be written as $\omega = \omega_0 + bt + \frac{1}{2} \hat{b} t^2 + ...$, where $\omega_0$ is the central frequency of the electric field while $b$ and $\hat{b}$ are the linear and quadratic chirp parameters, respectively.

\(^4\) $n = 1$ for the molecular beam in the vacuum chamber.
CHAPTER 2. COHERENT CONTROL OF CSCL DISSOCIATION

2.2.1 Potential curves of CsCl

In Fig. 2.2 the relevant potential curves of CsCl are depicted. The ground electronic state (X $^1\Sigma^+$) corresponds to ionically bound Cs$^+$ and Cl$^-$ and is modelled by a Rittner potential [48],

$$V_0(Q) = Ae^{-b(Q-R_e)} - B\frac{R_e}{Q} + E_0,$$  \hspace{1cm} (2.4)

where $Q$ denotes the internuclear distance between Cs and Cl. The asymptotic energy of the ground state $E_0$ is 0.27 eV corresponding to the energy difference of the ionization potential $E_{\text{ion}}$ of the Cs atom (3.89 eV, Ref. [53]) and the electron affinity of the Cl atom (3.616 eV, Ref. [54]). The parameters $A$, $b$, and $B$ were fitted to spectroscopic data, i.e. to the frequency of the ground state vibrations, 214 cm$^{-1}$ [53], and to the resonant transition at equilibrium internuclear separation, $R_e$ (2.906 Å, Ref. [54]), between the ground state and the first excited state, which corresponds to a wavelength of 250 nm [55].

The first and second excited electronic states A and B are repulsive and correspond to covalent bound Cs and Cl atoms. The asymptotic atomic states of Cl for the upper states (first and second excited state, continuum) are in all cases $3^2P$. Therefore the Cl states are omitted in all further considerations. The corresponding asymptotic atomic states of Cs are $6^2S_{1/2}$ and $7^2P_{1/2}$ with the asymptotic energies $E_1$ and $E_2$ of 0 eV and 2.70 eV, respectively [56]. The excited states are modelled by Born-Mayer potentials [55] of the same shape but with different asymptotic values, $E_n$ (see Table 2.1),

$$V_n(Q) = Ce^{-d(Q-R_e)} + E_n, \quad n = 1, 2.$$  \hspace{1cm} (2.5)

The potential parameters $C$ and $d$ are given for $V_1$ in Ref. [55]. Since no spectroscopic data are available for $V_2$, the $C$ and $d$ values of $V_1$ were used for $V_2$. This choice is nevertheless verified by the comparison between the computed and the measured pump-probe signals (see below).

The ionic potential $V_{\text{ion}}$ which models the continuum C is described by the following potential [57] with the asymptotic energy, $E_{\text{ion}}$:

$$V_{\text{ion}}(Q) = C_{\text{ion}}e^{-b_{\text{ion}}(Q-R_e)} - \frac{e^2\alpha_p}{8\pi\varepsilon_0 Q^4} + E_{\text{ion}},$$  \hspace{1cm} (2.6)

where $e$ denotes the charge of the electron and $\alpha_p$ corresponds to the polarizability of the neutral Cl atom. Except $E_{\text{ion}}$ all the parameters of the ionic potential curve were fitted in order to reproduce the adiabatic ionization potential, 8.28 eV [58] and the vertical ionization potential, 8.54 eV [59] of CsCl. In order to achieve this, $\alpha_p$ had to be
chosen unphysically large.\footnote{The second term on the right hand side of Eq. 2.6 takes into account a possible small contribution of a covalent bond between the Cs$^+$ ion and neutral Cl atom. This is analogous to the isoelectric molecule XeCl.} The results of the simulations are, however, not sensitive to a modification of these parameters in a relatively large range. This is due to the fact that ionization with the laser pulses considered in the present work always ends up far above the ionization limit. Potential parameters are summarized in Table 2.1.

### 2.2.2 Schrödinger equation

In order to simulate molecular dynamics properly, i.e., to fulfill selection rules, the degeneracy of the excited states (see Fig. 2.2) has to be resolved and the states of different symmetries ("+" and "−", referring to the total parity of the states) has to be treated separately. Hence, both the excited states and the continuum consist of two different states as shown in Fig. 2.3.\footnote{In our model we consider only singlet-singlet transitions. Furthermore we use the nomenclature belonging to Hund’s coupling case ‘a’ in the present considerations.} Since the treatment for "+" and for "−" parity initial states is the same, we consider here only initial states of "+" parity (even total angular momentum \(J\)). Denoting the wavefunction on the discrete level \(j\) with symmetry property \(\alpha\) by \(\Psi^\alpha_j(Q,t)\) and denoting the ionic wavefunction with energy \(E\) and symmetry property \(\alpha\) by \(\Psi^\alpha_{\text{ion}}(E,Q,t)\) the time-dependent Schrödinger equation (TDSE) may be expressed as follows:

\[
i \hbar \partial_t \Psi^\alpha_j(Q,t) = \left( \hat{T} + \hat{V}_j(Q) \right) \Psi^\alpha_j(Q,t)
- \varepsilon(t) \left( \int_0^\infty \mu_j^{\alpha,\beta}(E) \Psi^\beta_{\text{ion}}(E,Q,t) dE + \sum_{k=0}^2 \mu_j^{\alpha,\beta}_{k} \Psi^\beta_k(Q,t) \right)
\]

\[
i \hbar \partial_t \Psi^\alpha_{\text{ion}}(E,Q,t) = \left( \hat{T} + \hat{V}_{\text{ion}}(Q) + E \right) \Psi^\alpha_{\text{ion}}(E,Q,t) - \sum_{k=0}^2 \varepsilon(t) \mu_k^{\alpha,\beta}(E) \Psi^\beta_k(Q,t)
\]

Table 2.1: Parameters of the CsCl potentials and the reduced mass, \(m\) of the molecule, used in the simulations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td>0.59046 eV</td>
</tr>
<tr>
<td>(b)</td>
<td>3.19298 Å⁻¹</td>
</tr>
<tr>
<td>(R_e)</td>
<td>2.906 Å</td>
</tr>
<tr>
<td>(B)</td>
<td>5.47876 eV</td>
</tr>
<tr>
<td>(E_0)</td>
<td>0.274 eV</td>
</tr>
<tr>
<td>(C)</td>
<td>0.35 eV</td>
</tr>
<tr>
<td>(d)</td>
<td>3.6 Å⁻¹</td>
</tr>
<tr>
<td>(E_1)</td>
<td>0 eV</td>
</tr>
<tr>
<td>(E_2)</td>
<td>2.7 eV</td>
</tr>
<tr>
<td>(C_{\text{ion}})</td>
<td>0.8 eV</td>
</tr>
<tr>
<td>(b_{\text{ion}})</td>
<td>2.88 Å⁻¹</td>
</tr>
<tr>
<td>(\alpha_p)</td>
<td>7.42 Å³</td>
</tr>
<tr>
<td>(E_{\text{ion}})</td>
<td>3.89 eV</td>
</tr>
<tr>
<td>(m)</td>
<td>27.988 amu</td>
</tr>
</tbody>
</table>
where $\hat{T}$ denotes the kinetic part of the Hamiltonian operator, $\hat{V}_j(Q)$ and $\hat{V}_{\text{ion}}(Q)$ are the potential curves belonging to the discrete level $j$ and the ionic state, respectively. The electric field of the laser pulses is represented by $\varepsilon(t)$. In case of the two pulse simulations $\varepsilon(t)$ is the sum of the electric fields $\varepsilon_1(t)$ and $\varepsilon_2(t)$, described by Eq. 2.1 with the corresponding two different sets of parameters $\omega, I_0, t_0$ and $\tau$. As seen from the Eqs. 2.7 we used the same potential curves for both the ”+” and the ”−” states. Both the $\alpha$ and the $\beta$ may refer either to ”+” or ”−” states with the restriction that if $\alpha$ is ”+” then $\beta$ should be ”−” within the same equation and vice versa. The $\mu_{j,k}^{\alpha,\beta}$ denotes the transition dipole moment between discrete states $j$ with symmetry property $\alpha$ and $k$ with symmetry property $\beta$. Similarly $\mu_{j,k}^{\alpha,\beta}(E)$ denotes the transition dipole moment distribution between discrete state $i$ with symmetry $\alpha$ and the continuum of symmetry $\beta$. We make the following assumptions:

\begin{equation}
\mu_{j,k}^{+,-} = \mu_{k,j}^{-,+} = \mu_{j,k} \quad j, k = 0, \ldots, 2 \tag{2.8a}
\end{equation}

\begin{equation}
\mu_{j,j}^{+,-}(E) = \mu_{j,j}^{-,+}(E) = \mu_{j}(E) \quad j = 1, 2 \tag{2.8b}
\end{equation}

and as discussed before, $\mu_{j,k}^{\alpha,\alpha} = \mu_{j}^{\alpha,\alpha}(E) = 0$ for all possible $j, k$ and $\alpha$. Transition dipole moments other than those shown in Fig. 2.3 were taken to be zero, because the corresponding transition energies do not match the photon-energies.

### 2.2.3 Transition dipole moments

In this section the calculation of the transition dipole moments $\mu_{j,k}$ between discrete electronic levels with asymptotic energies $E_j$ and $E_k$ (see Fig. 2.2) and the transition dipole moment distributions $\mu_{j}(E)$ between a discrete state $j$ and the continuum state with energy $E$ are given for the allowed transitions (see Fig. 2.3).

The transition dipole moments $\mu_{01}$ and $\mu_{02}$ were calculated from oscillator strengths, $f_{nm}$ according to the relation [60]

\begin{equation}
|\mu_{nm}|^2 = \frac{3e^2\hbar}{2m_\text{e}\omega_{nm}} f_{nm} \tag{2.9}
\end{equation}

where $\omega_{nm}$ is the resonance frequency between level $n$ and $m$, and $m_\text{e}$ is the mass of the electron. The transition dipole moment $\mu_{01}$ was calculated using the value of $(0.065\pm0.008)$ for $f_{01}$ of the CsCl molecule [55]. In the calculation of $\mu_{02}$ we approximated the $f_{02}$ by the value of $f_{01}$ and used the resonance frequency $\omega_{02} = 1.178 \cdot 10^{16}$ Hz. For $\mu_{12}$ we used the transition dipole moment corresponding to the transition $6s \rightarrow 7p$ of the Cs atom given in [61].
The transition dipole moment distributions $\mu_1(E)$ and $\mu_2(E)$ have to vanish for infinite photon energies, therefore, a cutoff energy $E_{\text{max}}$ is introduced. For energies larger than $E_{\text{max}}$ the distributions $\mu_1(E)$ and $\mu_2(E)$ were set to zero, whereas in the energy range of $0 \leq E \leq E_{\text{max}}$ they were assumed to be constant and equal to the nonzero values $\mu_1$ and $\mu_2$, respectively. This kind of distribution that is usually used in the literature [62, 63], was chosen since it makes a convenient discretization of the continuum possible and thus makes the numerical solution of Eq. 2.7 feasible (see later). The value for $E_{\text{max}}$ has to be chosen carefully in order not to truncate the spectral tail of the laser pulses when simulating the ionization process. The values for $\mu_1$ and $\mu_2$ were calculated with the help of the measured one- and two-photon ionization cross-sections, $\sigma_1^{(1)}$ and $\sigma_1^{(2)}$ of atomic Cs. According to [64] starting from the expression for the one-photon transition cross section [65] the following equation can be deduced for the relation between the one-photon ionization cross-section $\sigma_1^{(1)}$ and the corresponding $\mu_1$:

$$\sigma_1^{(1)} = \frac{4\pi^2\alpha E_{\text{photon}}}{e^2} |\mu_1|^2$$

where $\alpha$ denotes the fine structure constant. The value of $6.9 \cdot 10^{-20}$ cm$^2$ for $\sigma_1^{(1)}$ at a wavelength of 248 nm [66] results in a value of $8.79 \cdot 10^{-22}$ Cm/J$^{-1/2}$ for $\mu_1$.

The $\mu_2$ was estimated with the help of the two-photon ionisation cross section, $\sigma_1^{(2)}$ of the Cs atom, using the relation $P_1^{(2)} = \sigma_1^{(2)} \Phi^2$ between transition probability $P_1^{(2)}$ and photon flux $\Phi$. According to [64] starting from the expression for the two-photon transition probability given in [67] the following relation can be deduced for $P_1^{(2)}$:

$$P_1^{(2)} = \hbar \left( \frac{2\pi\alpha \Phi E_{\text{photon}}}{e^2} \right)^2 \left| \sum_{\beta} \frac{\mu_{1\beta} \mu_{\beta}}{E_{1\beta} - E_{\text{photon}}} \right|^2$$

Figure 2.3: The transition dipole moments $\mu_{jk}$ between the discrete states $j$ and $k$ in addition to the transition dipole moment distributions $\mu_i$ between the discrete state $i$ and the continuum are shown and indicated by arrows for an initial state of “+” symmetry. Taking the selection rules for the parity as well as the one for J into consideration, we can see that both A$^-$ and B$^-$ may denote $1\Sigma^+_0$ and $1\Pi_1$ states. A$^+$ may denote $1\Sigma^+_0$, $1\Sigma^-_0$ and $1\Pi_1$ states, whereas B$^+$ may also denote $1\Delta_2$ state.
where $E_{1\beta}$ corresponds to the transition energy between states 1 and $\beta$. In general, the summation in eq. 2.11 should run over all intermediate states $\beta$ between state 1 and the continuum. Practically the contributions of intermediate levels with large energy differences $|E_{1\beta} - E_{\text{photon}}|$ to the transition probability, may be neglected. Hence, to obtain $\mu_2$, only the intermediate level $\beta = 2$ (the B state of our model) was taken into consideration which asymptotically corresponds to the 7$p$ state of the atomic Cs and thus the energy difference 2.7 eV between state A and state B is the closest to resonance with respect to the photon energy, 2.5 eV of our VIS pulses. Using the value of $2.6 \cdot 10^{-50}$ cm$^4$s given by [68] for the ionization cross section $\sigma_1^{(2)}$ of the Cs atom from its ground (6$s$) state for photon energy 20000 cm$^{-1}$ (2.48 eV) at an intensity of $I = 0.1$ TW/cm$^2$ one obtains $1.64 \cdot 10^9$ s$^{-1}$ for $P_1^{(2)}$. Since $\mu_{12}$ is already obtained from Eq. 2.9, Eq. 2.11 results in a value of $9.06 \cdot 10^{-21}$ Cm/J$^{-1/2}$ for $\mu_2$. The calculated transition dipole moment values (together with the parameter $E_{\text{max}}$) used in the simulations are summarized in Table 2.2.

### Table 2.2: Transition dipole moments used in the simulations.

<table>
<thead>
<tr>
<th>$E_{\text{max}}$</th>
<th>5 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{01}$</td>
<td>$6.18 \cdot 10^{-30}$ Cm</td>
</tr>
<tr>
<td>$\mu_{02}$</td>
<td>$4.96 \cdot 10^{-30}$ Cm</td>
</tr>
<tr>
<td>$\mu_{12}$</td>
<td>$-3.12 \cdot 10^{-30}$ Cm</td>
</tr>
<tr>
<td>$\mu_1$</td>
<td>$8.79 \cdot 10^{-22}$ Cm/J$^{-1/2}$</td>
</tr>
<tr>
<td>$\mu_2$</td>
<td>$9.06 \cdot 10^{-21}$ Cm/J$^{-1/2}$</td>
</tr>
</tbody>
</table>

2.3 Numerical methods

In contrast to a discrete level and due to the continuous distribution of the kinetic energy of the emitted electron, the TDSE governing the photoionisation process is expressed by an uncountably infinite set of differential equations (see Eqs. 2.7). Thus a special treatment was needed to solve the TDSE in this case. The most convenient way to do this numerically is the method of discretizing the electronic continuum proposed by Burkey and Cantrell [62, 63]. The aim of this discretization is to replace the uncountably infinite set of differential equations by a countably infinite set of differential equations. The method is based on an expansion of the energy dependent ionic wavefunction $\Psi_{\text{ion}}(E, Q, t)$ in terms of proper polynomials of the kinetic energy, $E$ of the emitted electron. This series of expansion is then truncated resulting in a finite number of differential equations that can
be treated numerically. Truncation, however, may lead to erroneous results if not enough
terms are kept in the series of expansion. The number of terms to be kept is determined
by a tradeoff between errors due to the truncation and computation time. Therefore,
methods, which are able to reduce the number of terms without increasing the error are
desired. In this section such techniques are discussed and investigated numerically. First
the method of discretizing the continuum is described then the conventional- as well as
the suggested novel method to avoid errors originating from the truncation are discussed
and investigated numerically on a simple two-level system. Finally the application of these
numerical methods to the model of the CsCl is discussed.

2.3.1 Discretization of the continuum

For the sake of simplicity a simple model system for a brief discussion of the problem and
for the demonstration of the method was used. This model system consists of only one
discrete electronic level and one ionisation continuum describing a hypothetical diatomic
molecule. The space- and time-dependent wavefunctions corresponding to the discrete
level and to the ionisation continuum are denoted by $\Psi_0(Q, t)$ and $\Psi_{\text{ion}}(E, Q, t)$, respectively. The transition dipole moment distribution $\mu(E)$ is assumed to be independent of
the internuclear distance. Since $|\mu(E)|^2$ has to vanish for infinite energy $E$ a cutoff energy
$E_{\text{max}}$ is introduced and $\mu(E)$ is defined in the following way: $\mu(E) = \mu$ if $0 < E < E_{\text{max}}$
and $\mu(E) = 0$ otherwise. The only constrain concerning $E_{\text{max}}$ is that it should be chosen
large enough not to truncate the ionisation artificially at the spectral tails of the laser
pulses. The appropriate orthogonal polynomials for the above defined dipole-moment distri-
bution $\mu(E)$ are the Legendre polynomials $P_l(x)$ [51]. With a proper choice of their
arguments and with an additional multiplication factor these polynoimals can be trans-
formed to a system of polynomials orthonormal in the interval $[0, E_{\text{max}}]$. The continuum
wavefunction can be well approximated by a truncated series of these polynomials when
laser pulses of finite duration are considered [51]. The space- and time-dependent coeffi-
cients of the polynomials are represented by $\Phi_l(Q, t)$ with indices $l > 0$. Using only $M + 1$
terms in the finite expansion the ionic wavefunction $\Psi_{\text{ion}}(E, Q, t)$ can be expressed as
follows

$$
\Psi_{\text{ion}}(E, Q, t) = \sum_{l=0}^{M} \Phi_{l+1}(Q, t) \sqrt{\frac{2l+1}{E_{\text{max}}}} P_l \left( \frac{2E}{E_{\text{max}}} - 1 \right).
$$

(2.12)
Substituting the above expression into the TDSE and using the well known recursion relations for Legendre polynomials the TDSE has the form:

\[
i\hbar \frac{\partial}{\partial t} \Psi_0(Q, t) = [\hat{T} + \hat{V}_0(Q)] \Psi_0(Q, t) - \varepsilon(t) \mu \sqrt{E_{\text{max}}} \Phi_1(Q, t) \tag{2.13a}
\]

\[
i\hbar \frac{\partial}{\partial t} \Phi_1(Q, t) = \left[\hat{T} + \hat{V}_\text{ion}(Q) + \frac{E_{\text{max}}}{2}\right] \Phi_1(Q, t) - \varepsilon(t) \mu \sqrt{E_{\text{max}}} \Psi_0(Q, t) + \frac{E_{\text{max}}}{2\sqrt{3}} \Phi_2(Q, t) \tag{2.13b}
\]

\[
i\hbar \frac{\partial}{\partial t} \Phi_l(Q, t) = \left[\hat{T} + \hat{V}_\text{ion}(Q) + \frac{E_{\text{max}}}{2}\right] \Phi_l(Q, t) + \frac{E_{\text{max}}}{2} \left[a_l \Phi_{l-1}(Q, t) + a_{l+1} \Phi_{l+1}(Q, t)\right], \tag{2.13c}
\]

where \(l = 2, \ldots, M\), \(\hat{T}\) denotes the kinetic part of the Hamiltonian operator, and \(\hat{V}_0(Q)\) and \(\hat{V}_\text{ion}(Q)\) are the potential curves belonging to the discrete level and the ionic state, respectively. \(a_l\) is defined as

\[
a_l = \frac{l - 1}{\sqrt{4(l - 1)^2 - 1}} \tag{2.14}
\]

It is apparent that the discrete electronic state in this representation is coupled only with the lowest continuum coefficient, \(\Phi_1\), and each continuum coefficient is coupled only to its nearest neighbors. Thus, the continuum is represented by a ladder of continuum coefficients and population of the lowest coefficient can migrate only step by step to coefficients of higher indices. In order to reveal the behaviour of the continuum coefficients \(\Phi_l(Q, t)\) \((l > 1)\) not directly coupled to the discrete state we consider Eq. (2.13c), approximate all \(a_l\) by their asymptotic value of \(1/2\) (see Eq. (2.14)), and write the solution in the following form

\[
\Phi_l(Q, t) = s(Q, t) * c_l(t). \tag{2.15}
\]

If \(s(Q, t)\) fulfills the equation

\[
i\hbar \frac{\partial}{\partial t} s(Q, t) = \left[\hat{T} + \hat{V}_\text{ion}(Q) + \frac{E_{\text{max}}}{2}\right] s(Q, t) \tag{2.16}
\]

which is the TDSE describing a free propagation on the ionic potential then the equation governing the time evolution of the amplitudes \(c_l(t)\) of the continuum coefficients is approximated by the expression

\[
i \frac{\partial}{\partial t} c_l = \frac{E_{\text{max}}}{4\hbar} (c_{l+1} + c_{l-1}). \tag{2.17}
\]

This equation investigated thoroughly by Burkey [62] and Seel [51] has a solution of a propagating wave:

\[
c_l(t) \propto e^{-i(\Omega t \pm Kl)}, \tag{2.18}
\]
where the wavenumber $K$ is determined by the source of the waves, i.e. by the exciting pulse responsible for populating the lowest continuum coefficient. The group velocity, $v_g$, of this propagation is

$$v_g = \frac{\partial \Omega}{\partial K} = \pm \frac{E_{\text{max}}}{2\hbar} \sin K.$$  \hspace{1cm} (2.19)

As mentioned in reference [63] slowly spreading wave packets will have the maximum or minimum values, namely, $v_g = \pm E_{\text{max}}/2\hbar$. Considering an infinite ladder the exciting laser pulse can result only in an outward propagating wavepacket. The continuous outflow of population from the lowest continuum coefficient, i.e., from the only coefficient connected to the discrete levels, ensures that no depumping occurs from the continuum to the discrete levels. Ideally, after the exciting laser pulse ceases no population is found on the lowest continuum coefficient. Since in numerical simulations only a finite number of continuum coefficients can be considered it may happen that the wavepacket propagating initially towards coefficients of higher indices is reflected back at the end of the ladder and is propagating backwards. If it reaches the lowest continuum coefficient while an electric field is still present population is depumped leading to incorrect results. Therefore, back-reflection must be avoided.

### 2.3.2 Methods to avoid backreflection

The most common way to avoid back-reflection is to involve so many continuum coefficients in the computations that backward propagating population can not reach the lowest coefficient while an electric field is present. In the following text this method will be referred as the ‘exact’ method. The actual number of continuum coefficients required by this method is determined by the duration of the pulses to be simulated and the group velocity, $v_g$. However, the time consumption of the simulations drastically increases when pump-probe measurements are simulated with pulses of some tens or some hundreds of femtoseconds pulse duration with some hundreds of femtoseconds time delays between them. The situation is even worse if the spatial evolution of the wavepackets has to be followed and thus hundreds or thousands of spatial grid points have to be considered.

In those cases when only the total amount of continuum population has to be determined or one is rather interested in the residual population distribution on discrete levels (and not the photoelectron spectra for example) one can add a dissipating potential (DP), $\hat{V}_{l}^{(\text{dis})}$, to $\hat{V}_{\text{ion}}(Q)$ in the Hamiltonian in Eq. (2.13). The purpose of the dissipating potential is to decay the population exponentially in time during its migration from continuum coefficients of lower indices towards higher ones, thus, avoiding back-reflection (such a
DP has been used as an absorbing boundary for the one dimensional TDSE which — except from the corresponding dispersion relations — has a very similar form to Eq. (2.17) [69, 70]. A DP similar to the one investigated by Neuhauser and Baer [70] can be defined in the following way

$$\hat{V}_l^{(dis)} = -i \frac{\hbar}{dt} \beta (l - 1), \quad (2.20)$$

where \(l \geq 1\) and \(dt\) denotes the time step used in the numerical simulation. \(\beta\) is a small positive constant parameter which determines the decay of the DP and thus the decay of the population during its propagation towards continuum coefficients of higher indices. Using a DP results in loosing continuum population in the simulations, thus, the real value of continuum population is calculated by subtracting the sum of the populations on the discrete electronic levels from the initial overall population.

Since the time needed for simulating molecular dynamics can be extremely large an even further reduction of continuum coefficients is appreciated even at the expense of precision. Hence, a non-reflecting boundary condition (NRBC) for the semi-discrete partial differential equation Eq. (2.17) was developed. Such NRBC’s were thoroughly investigated for various problems by Givoli [71]. Non-reflecting boundary conditions for the TDSE (that has a very similar form to Eq. (2.17)) were also developed and discussed in the literature [72, 73, 74]. An exact boundary condition non-local in time [73] which was developed for the one-dimensional TDSE using the Green function method can be applied to the present problem provided that the potential curves of the ionic state and the discrete states are of the same shape. In this case the spatially dependent part of the wavefunctions can be separated. In general (i.e. for different potential curves), the exact NRBC is neither local in time nor in space but it is related to the derivatives of the wave function at the ladder boundary [74]. Since the increase of the computational time due to the application of such an exact NRBC would be relatively large an approximate NRBC local both in time and in space is needed.

Such an approximate NRBC has not yet been applied for the ionization problem, but emerges directly under the assumption that the wave packet spreads slowly and thus it propagates with the maximum group velocity, \(E^{\text{max}} / 2 \hbar\). From Eqs. (2.18) and (2.19) then it follows for an outgoing wave, that

$$-2 i c_l = c_{l+1} - c_{l-1} \quad (2.21)$$

and thus the last continuum coefficient \(\Phi_{M+1}\) has to be determined for all \(t\) and \(Q\) as

$$\Phi_{M+1}(Q,t) = \Phi_{M-1}(Q,t) - 2 i \Phi_M(Q,t). \quad (2.22)$$
Eq. (2.22) is the boundary condition applied in the numerical simulations and in the following NRBC refers to this equation.

### 2.3.3 Numerical investigation of the NRBC method

To demonstrate the feasibility of the NRBC (Eq. (2.22)) in order to avoid back reflection at the ladder boundary numerical simulations with three different methods, i.e. using a large number of continuum coefficients (‘exact’ solution), a dissipating potential, and the NRBC were performed on a two-level model system.

For these calculations the ground electronic state, $\hat{V}_0(Q)$, of the CsCl molecule was used and the potential curve, $\hat{V}_{\text{ion}}(Q)$, had in this case the same shape as $\hat{V}_0(Q)$ but shifted by an ionisation energy, $E_{\text{ion}}$, i.e. $\hat{V}_{\text{ion}}(Q) = \hat{V}_0(Q) + E_{\text{ion}}$. The $E_{\text{ion}}$ and the $\mu \sqrt{E_{\text{max}}}$ were in this case taken as 4 eV and 1 au, respectively. All the other parameters of the potentials as well as the reduced mass $m$ used in the simulations were the same as listed in Table 2.1. The initial wavefunction was again the vibrational ground state of $\hat{V}_0(Q)$. A bandwidth limited Gaussian pulse with a full width at half maximum (FWHM) of 20 fs, a peak intensity of 2 TW/cm$^2$, and a central wavelength of 247.5 nm (corresponding to a photon energy of 5 eV) was used. The pulse was centered at 44 fs. The time step and the grid spacing were 0.03 fs and 0.00125 Å, respectively. The minimum internuclear distance was 1.9 Å. The number of time steps and the number of spatial grid points were 3000 and 2048, respectively. $E_{\text{max}}$ was chosen to 2 eV, so that the center frequency of the pulse equals $E_{\text{ion}} + E_{\text{max}}/2$.

First, simulations with $M = 50$ continuum coefficients were performed. In this case the back-reflected population could not reach the lowest coefficient before the pulse ceased. The time evolution of the population on several continuum coefficients is displayed in Fig. 2.4(a). The migration of population towards coefficients of larger indices as well as the effect of back reflection for large times are clearly seen. Results of simulation with $M = 15$ continuum coefficients using the DP with $\beta = 0.00153$ are displayed in Fig. 2.4(b). Clearly, the decay of the population with increasing index of coefficients can be seen. Unlike the previous case no back reflection is observable. Results of simulations with only $M = 5$ coefficients using the NRBC (Eq. (2.22)) are shown in Fig. 2.4(c). Obviously, and similar to the second case using the DP back reflection is avoided. The time evolution of the population on the lowest continuum coefficient is almost the same in all the three cases up to 75 fs, i.e. during the effect of the laser pulse.

In Fig. 2.5 the time evolution of the population on the discrete level is shown. Curve
(a) corresponds to the ’exact’ solution and curve (b) to a simulation with only $M = 2$ continuum coefficients. Clearly, the back reflection causes a totally wrong result. Curves (c) and (d) correspond to simulations with $M = 2$ continuum coefficients using a DP ($\beta = 0.015$) and the NRBC, respectively. In comparison to curve (b) a dramatic improvement is seen and in addition it is obvious that the NRBC comes closest to the ’exact’ solution. In Table 2.3 the computation time for one simulation is listed for different numbers of continuum coefficients.

These examples show that the NRBC is an appropriate tool for solving the TDSE using a small number of continuum coefficients. In order to get a more detailed insight to the problem, the precision of computations with the NRBC was investigated as a function of different parameters. In these investigations we eliminated the spatial dependence in order to save computational time. This elimination was possible due to the identical shape of the potential curves. First, the precision of the computations as a function of the number of continuum coefficients was investigated. The final populations on the discrete level for different numbers of continuum coefficients were compared to the final population
Figure 2.5: Time evolution of the population on the discrete level for different simulations. Curve (a) corresponds to the 'exact' solution, i.e. to a simulation using a large number \((M = 60)\) of continuum coefficients. Curves (b) – (d) were obtained using \(M = 2\) continuum coefficients. Curve (b) belongs to a simulation when neither a DP nor the NRBC was applied. Curve (c) shows the results of a simulation using the DP with \(\beta = 0.015\) and curve (d) corresponds to the simulation using the NRBC.

\[
\begin{array}{|c|c|}
\hline
M & \text{CPU time (min)} \\
\hline
2 & 1.2 \\
5 & 3.08 \\
8 & 5.8 \\
10 & 8.1 \\
15 & 15 \\
50 & 202 \\
\hline
\end{array}
\]

Table 2.3: Computation time of one simulation for different numbers of continuum coefficients \(M\) (The total number of levels including the discrete level is equal to \(M + 2\)).

obtained by the 'exact' method. The relative differences are shown in Fig. 2.6(a). As expected, the deviation was the largest for \(M = 2\) continuum coefficients. However, even in the worst case the deviation was only slightly larger then 5%. The error may partially be due to the fact that for continuum coefficients of low indices the approximation Eq. (2.17) is not valid. In order to demonstrate the advantage of the NRBC method compared to the DP method the precision of the computations with the DP for various numbers of continuum coefficients was investigated. The relative error of the residual population of the discrete state was determined as a function of the decay parameter, \(\beta\). The results of these simulations are shown in Fig. 2.6(b). The numbers next to the curves denote the corresponding values of \(M\). As can be seen, there exists an optimal decay for a certain excitation and the error of the computation can even be equal to zero for odd \(M\) values — even for low \(M\). However, the error can not be minimized for a wide range of pulse parameters, since the optimal \(\beta\) strongly depends on the exciting pulse when only a few
continuum coefficients are involved. This behaviour is shown in Fig. 2.7(a).

![Figure 2.6](image-url)

Figure 2.6: Dependence of the computational error on the number of continuum coefficients for the NRBC- and DP-method and on the parameter $\beta$ for the DP-method. In both subfigures the relative error of the final population on the discrete level with respect to the 'exact' solutions is displayed. (a) shows the results of simulations using the NRBC for an excitation with a pulse of 20 fs FWHM and 2 TW/cm$^2$ peak intensity as a function of the number of continuum coefficients. (b) shows the results of simulations using the DP for an excitation with a pulse of 10 fs FWHM and 2 TW/cm$^2$ peak intensity as a function of decay parameter, $\beta$, for various numbers of continuum coefficients. The number $M$ of levels involved is indicated next to the corresponding curves.

The relative error for both the DP (dotted line) and the NRBC (solid line) methods using $M = 3$ continuum coefficients is shown as a function of the FWHM of the exciting pulse (peak intensity: 2 TW/cm$^2$). For simulations using the DP $\beta$ was equal to 0.0087. This value is optimal for a FWHM of about 8 fs but results in an error much larger than that obtained by the NRBC method for other FWHM values. Hence, in order to obtain reliable results for arbitrary excitation one has to involve a larger number of continuum coefficients using the DP method with a suitably small decay parameter, $\beta$. In addition, the dependence of the errors caused by both methods on the peak intensity was investigated. $M = 3$ continuum coefficients were used. Fig. 2.7(b) shows the relative error of the residual population on the discrete level as a function of the peak intensity (FWHM: 10 fs). Although the peak intensity changes by more than two orders of magnitude the relative error in the case of the NRBC remains below 2%. Similar to Fig. 2.7(a) the range where the DP method overcomes the NRBC method is limited and a relatively low computational error may be obtained in a wider range of pulse parameters for the NRBC method than for the DP method.
Figure 2.7: Dependence of the computational error of the final population on the laser pulse parameters. Figures (a) and (b) display the relative error of the residual population on the discrete level obtained by simulations with $M = 3$ continuum coefficients as a function of the FWHM (with a constant peak intensity of 2 TW/cm$^2$) and of the peak intensity (with a constant FWHM of 10 fs), respectively. The solid curves correspond to simulations with the NRBC whereas the dotted curves correspond to simulations using a DP with a decay parameter $\beta$ of 0.0087.

In summary, the attractive features of the NRBC given by Eq. 2.22 are that it is local both in time and in space, thus requires no a priori knowledge on the excitation process and it has no parameter to adjust contrary to the DP-method. As the two other methods, the NRBC is also restricted to cases when the transition dipole moment can be approximated by a constant value within a certain energy interval. Using the NRBC a considerable reduction in the computational time can be achieved. This may be essential in cases when: I) Both the spatial and the temporal dynamics have to be simulated and the rotating wave approximation can not be used for some reason. These cases require a high spatial and temporal resolution. II) Relatively long pulses have to be considered in the simulations. III) The computation has to be repeated several times with different pulse parameters. IV) Ionisation to multiple continua has to be considered. Simulating the pump-probe experiment on the CsCl according to the model presented in section 2.2 is just that kind of task.
2.3.4 Schrödinger equation for CsCl

Starting from Eq. 2.7, and using the method of continuum-discretization the final form of the Schrödinger equations corresponding to our model of the CsCl is given as

\[ i \hbar \frac{\partial}{\partial t} \Psi_{j}^{\alpha}(Q, t) = [\hat{T} + \hat{V}_{j}(Q)] \Psi_{j}^{\alpha}(Q, t) - \varepsilon(t) \tilde{\mu}_{j}^{\alpha,\beta} \Phi_{1}^{\beta}(Q, t) - \varepsilon(t) \sum_{k=0}^{2} \mu_{jk}^{\alpha,\beta} \Psi_{k}^{\beta}(Q, t) \] (2.23a)

\[ i \hbar \frac{\partial}{\partial t} \Phi_{1}^{\alpha}(Q, t) = \hat{H}_{\text{ion}}(Q) \Phi_{1}^{\alpha}(Q, t) - \varepsilon(t) \sum_{k=1}^{2} \tilde{\mu}_{k}^{\alpha,\beta} \Psi_{k}^{\beta}(Q, t) + \frac{E_{\text{max}}}{2\sqrt{3}} \Phi_{2}^{\alpha}(Q, t) \] (2.23b)

\[ i \hbar \frac{\partial}{\partial t} \Phi_{l}^{\alpha}(Q, t) = \hat{H}_{\text{ion}}(Q) \Phi_{l}^{\alpha}(Q, t) + \frac{E_{\text{max}}}{2} [a_{l} \Phi_{l-1}^{\alpha}(Q, t) + a_{l+1} \Phi_{l+1}^{\alpha}(Q, t)] \] (2.23c)

where \( \tilde{\mu}_{j}^{\alpha,\beta} \) was introduced instead of \( \mu_{j}^{\alpha,\beta} \) in the following way

\[ \tilde{\mu}_{j}^{\alpha,\beta} = \mu_{j}^{\alpha,\beta} \sqrt{E_{\text{max}}} \quad j = 1, 2 \] (2.24)

and \( \hat{H}_{\text{ion}}(Q) \) is defined as

\[ \hat{H}_{\text{ion}}(Q) = \left[ \hat{T} + \hat{V}_{\text{ion}}(Q) + \frac{E_{\text{max}}}{2} \right] \] (2.25)

The indices \( j = 0, ..., 2 \) and \( l = 2, ..., M \) in Eqs. 2.23 stand - as before - for the discrete levels and for the continuum coefficients, respectively. \( a_{l} \) is defined in Eq. 2.14. All parameters used in the simulations are already summarized in Tables 2.1 and 2.2. The time step and the grid spacing were the same that we used for the model system, i.e., 0.03 fs and 0.00125 Å, respectively. The number of spatial grid points, however, had to be increased to 8192.

Unlike the previous model system, in case of the model of CsCl molecule the spatial and temporal evolution of the wavepacket can not be separated and simulations have to be performed on a larger spatial grid. Furthermore, in order to reproduce the experimental results (i.e., the pump-probe signal, see later) the simulations have to be performed several times for different delay times and laser pulse parameters, respectively. As a consequence the computational time increases and the simulations become even more time consuming since the pulses and the delays involved are comparatively long. Thus most of the numerical simulations for this model of the CsCl were performed using the NRBC with 4 continuum coefficients for each continuum, leading to a total number of 13 levels. (5 discrete levels plus two times 4 continuum coefficients.) However, as we have seen before, the NRBC method, relies on the assumption that the wavepacket on the continuum
Figure 2.8: Evolution of populations in the ground state and in the ionisation continuum of CsCl for a delay of 100 fs between the UV and VIS laser pulses. The continuum population in figure (a) is the sum of the populations in the two continua and its asymptotic value represents the Cs$^+$ ion signal at a delay of 100 fs. The ground state population is shown in figure (b). The results obtained for the NRBC are displayed with solid lines. Dashed lines display the results obtained with a DP using 15 continuum coefficients for each continuum and a damping factor $\beta = 0.00133$. As can be seen, both the time evolution and the asymptotic values are very much the same for both methods.

coefficients is slowly spreading. Instead of verifying this assumption in each case of simulating the pump-probe experiments on the CsCl-molecule, the NRBC was again tested by comparing its performance with that of the DP-method for some cases of delay times and pulse-parameters. No simulations were performed to obtain the ‘exact’ result for the model of the CsCl, since to perform the calculations with an appropriately large number of levels would have been too time consuming. Results of simulation with a DP using 15 continuum coefficients ($\beta = 0.00133$) and that of the NRBC are displayed in Fig. 2.8. The figure shows the temporal evolution of populations in the ground state and in the continuum for the two-pulse excitation. The UV pulse parameters are: 248.5 nm, 186 fs FWHM, 0.45 TW/cm$^2$ peak intensity. The visible laser pulse parameters are: 497 nm, 86 fs FWHM, 4.7 TW/cm$^2$ peak intensity. The UV and the VIS pulses are centered at 300 fs and 400 fs, respectively. The wavepacket dynamics and the underlying physical processes are discussed in detail in the next section.

Assuming that the results for the DP are close to the real values the error of the NRBC method is less than 5%. The time consumption of the computation, however, was more then 7 times less for the NRBC (13 levels in total) than for the DP (35 levels in total).

\footnote{A further increase of M or decrease of $\beta$ caused only minor changes in the population transfers.}
Figure 2.9: a) The Cs$^+$ ion signal produced only by the femtosecond UV pulse (denoted by 'UV' in the figure) is shown as a function of UV intensity. The slope of $(1.73 \pm 0.03)$ represents the two photon process. b) The ion signal is plotted versus the intensity of the UV. In addition, a XeCl pulse with an energy density of about 1.9 J/cm$^2$ is used in order to ionize neutral Cs. The slope of $(1.05 \pm 0.04)$ indicates a one photon excitation process by the UV. For higher UV intensities the onset of saturation of the signal may be seen, which results in a reduced slope with increasing signal.

As a further test of the NRBC method (and that of the whole numerical algorithm) is presented in appendix 5.1. There the probability of the ionization by the VIS pulse was computed according to a simple rate-equation for a large delay time and compared to the corresponding value obtained from the simulation with the NRBC.

2.4 Results of experiments and simulations on CsCl

2.4.1 One-photon processes

In this section investigations concerning the basic processes induced by the fs UV laser pulse alone are described. These investigations are necessary to support the assumptions of the theoretical model and to interpret correctly the molecular dynamics involved in the control process.

The results of two series of measurements can be seen in Fig. 2.9. The graphs are double
logarithmic in order to reveal the order of the photon processes involved. In Fig. 2.9 a) the Cs$^+$ ion signal produced by the fs UV laser pulse as a function of the pulse intensity is shown. (The fs UV pulse is denoted by 'UV' in the figure. Its pulse duration was $100 \pm 10$ fs). The underlying process is a two step excitation from the ground state to the first excited state and subsequently to the ionization continuum (By using the notations of Fig. 2.2 this means an X-A A-C transition). Thus, at low intensities a slope of 2 is expected. If, however, the intensities approach the saturation limit of the X-A transition the slope must decrease. Assuming that the lifetime of level A is longer than the pulse duration (100 fs) and using an absorption cross section of $1.6 \cdot 10^{-17}$ cm$^2$ given in Ref. [48] we get approximately 50 mJ/cm$^2$ saturation energy density for the X-A transition. If we compare this with the maximum UV energy density of 120 mJ/cm$^2$ used in the experiments we can anticipate that the measurements go well into the saturated range.

After the excitation the wave packet of the molecule moves very fast towards larger internuclear distances which means that the above ionization process is relatively inefficient and most of the molecules dissociate via the neutral channel. Thus, to obtain the saturation behavior of the X-A transition the yield of neutral Cs atoms needs to be measured. This was accomplished by using a standard (nanosecond) XeCl excimer laser pulse. The XeCl laser was chosen for two reasons. First, its photon energy of 4.03 eV is close to the ionization energy of the Cs atoms (3.89 eV, Ref [53]). Second, which is equally important, the photon energy is not enough to dissociate CsCl molecules. One expects a certain contribution due to two photon process but this was measured to be negligibly small. This can be understood considering that the pulse duration of the XeCl excimer laser is about $10^5$ times longer than that of the fs UV laser pulse resulting in $10^2$ lower intensity even when the energy density of the XeCl beam is about $10^3$ higher. In order to ensure that the ionization does not interfere with the molecular processes the XeCl pulse was delayed 50 ns with respect to the fs UV pulse.[23, 24]

In Fig. 2.9 b) the number of ionized Cs atoms is shown as a function of the fs UV laser intensity. (During the measurements the energy density of the ionizing XeCl beam was kept constant at 1.9 J/cm$^2$.) From the figure one can see that around the maximum UV intensities saturation of the X-A transition clearly occurs. The smaller slope in the upper part of the curve is fully consistent with the measured $(1.73 \pm 0.03)$ slope of the two photon ionization process (2.9 a)). The fact that the X-A transition reaches saturation is important because it supports the assumption that the CsCl control scheme operated in the strong response regime.

Intensity dependence of the ion signal was also investigated by numerical simulations. The
spatial intensity distribution, $I(\rho)$, across the beam profile in the focus was taken into consideration additionally. The $I(\rho)$ was assumed to be the same as defined in Eq. 2.3. The asymptotic continuum population $N_C(I)$ was computed by simulations for five different intensity values. Then a fifth order polynomial was fitted to these computed points to get a continuous $N_C(I)$ distribution. Finally the average over the spatial intensity distribution was computed analytically for five different peak intensities, $I_0$ according to the following formula

$$\int_0^\infty 2\rho \pi N_C(I(\rho)) \, d\rho .$$

(2.26)

Fig. 2.10 shows the results of these computations for UV pulses of 100 fs duration, just as in case of Fig. 2.9a). The slope of the curve for different UV intensities are indicated next to the curve. The decrease of the slope with the increase of the intensity is the effect of the saturation of transition $X \rightarrow A$. Nevertheless a linear fit to the five computed points shown by the dashed line in Fig. 2.10 results in a slope of 1.61, which is in satisfactory agreement with the measured value of 1.73 (cf. Fig. 2.9a)). It should be mentioned that ignoring the intensity distribution across the beam, would have resulted in a considerably lower slope of less than 1.4. On the other hand, taking also the effect of the uniform orientational distribution of the molecules into account in addition to the correction for the intensity distribution, an even better agreement between the computed and the measured slopes is expected.\(^8\)

In certain alkali-halides, such as NaI, the excited state wave packet dynamics is strongly

\(^8\)Assuming the same orientational dependence for the $A \rightarrow C$ as for the $X \rightarrow A$ transitions and using the corresponding formula of $\frac{1}{4\pi} \int_0^\pi d\beta \sin \beta \int_0^\infty d\rho 2\rho \pi N_C(I(\rho) \cos^2 \beta)$, where $\beta$ denotes the angle between the dipole moment and the electric field vectors, a linear slope of 1.69 is obtained. The minimum and the maximum values of the slope within the investigated intensity range are then 1.5 and 1.79, respectively.
influenced by the fact that there exists an intersection point between the ionic ground state (X) and the covalent excited state (A) potential. In such case the dissociation takes place via both the neutral and ionic channel with a branching ratio depending on the strength of the non-adiabatic coupling between the ionic and neutral potential curves at the intersection point. This is to first order proportional to the relative slopes of the two potential curves at the intersection point. The wave packet can be partially reflected back at the level crossing which eventually leads to wave packet oscillation on the excited potential surface (see Ref. [3]). In the case of CsCl the crossing appears at a relatively large internuclear distance of 51.4 Å [75]. The strength of the coupling and thus the branching ratio should, therefore, be negligibly small. The branching ratio between the dissociation channels was experimentally determined by measuring the number of CsCl atoms as a function of the ionizing XeCl laser energy density at constant fs UV intensity. The measured data (taken at a UV intensity of 0.1 TW/cm$^2$ and pulse width of (200 ± 20) fs) are indicated by dots in Fig. 2.11. The solid line represents a fit, from which an ionization cross section of $(17 \pm 2) \cdot 10^{-20}$ cm$^2$ for Cs is obtained at the XeCl wavelength of 308 nm. This is in excellent agreement with the $14.7 \cdot 10^{-20}$ cm$^2$ presented in Ref. [76]. Comparing the level of the Cs$^+$ signal at the maximum and at zero XeCl energy density one obtains 1:$(59 \pm 5)$ for the branching ratio of the ionic and neutral dissociation channel. It must be emphasized, however, that this is an upper bound because the measured value at zero XeCl energy is very likely overestimated due to the two photon ionization process discussed earlier and due to the presence of experimental noise. The conclusion that practically no dissociation takes place via the ionic channel is very important because of two reasons. First, it corroborates that the interaction at the crossing is very weak, and second, it
means that no wave packet oscillation on the excited state potential curve is expected. The identical measurements have been performed using the VIS laser pulses. Since the excitation from the ground state to the first excited state is a transition involving two VIS photons it is negligible compared to the influence of the UV photons on the excitation process.

2.4.2 Two-photon processes

After investigating the processes induced by isolated UV and VIS pulses the processes involved with the combination of the UV and VIS laser pulses is explored. The combination of the two fs laser pulses makes it possible to control the dissociation of CsCl. In Fig. 2.12 the measured Cs$^+$ ion signal versus the time delay between the UV and the VIS pulses is shown. Positive time delay always refers to the situation where the UV pulse precedes the VIS pulse.
Results of numerical simulation is presented in Fig. 2.12 by solid curves. The simulated Cs\textsuperscript{+} ion signal corresponds to the asymptotic population of the continuum (Fig. 2.14d)). As is seen in the figure, the simulated signal is in excellent agreement with the measured one. The calculated asymptotic populations of all other relevant CsCl states are plotted in Figs. 2.14a) to c). In the present case results of simulations are neither corrected for the intensity distribution of the laser beams nor for the orientation distribution of the molecules. While the lack of these averaging considerably influenced the results of simulations with one UV pulse of low intensities, its effect on the simulated pump-probe signal should be less important. One of the reasons for this is that the focus-diameter of the UV pulse is lower than that of the VIS one, so the intensity of the VIS pulse, which is mainly responsible for ionisation for positive delays, can be approximated by its maximum value, \( I_0^{VIS} \) within the whole beam-spot of the focused UV pulse. On the other hand the duration and the intensity of the UV pulse, used in the pump-probe measurements - as is clear from the previous investigations - are high enough to drive the induced X\( \rightarrow \)A transition deep into saturation. The effect of this saturation and that of the orientation distribution of the molecules will be tested later by computing the pump-probe signal with both the original- and the half of the peak intensities of the pulses.

The following wavepacket scenario illustrated in Fig. 2.13 explains the measured signal. The UV pulse transfers almost all of the ground state wavepacket to the first excited state A via a one photon process (see inversion of population in Fig. 2.14a) and b) at time delay -150 fs). Due to the repulsive nature of potential A, the wavepacket starts to...
Figure 2.14: The figures a) to d) show the asymptotic populations on the different states depending on the time delay between UV and VIS pulses as a result of numerical simulations. The sum of all the asymptotic populations for each time delay is normalized to unity. The continuum population in figure d) represents the Cs$^+$ ion signal already shown in Fig. 2.12. The identical pulse parameters as in Fig. 2.12 have been used.

propagate towards larger internuclear separations and is subjected to dispersion which leads to a broadening of the wavepacket. For positive delay times the VIS pulse can ionize the moving wavepacket to the continuum C by two photon absorption (see increase of populations in Fig. 2.14d) in the range -100 fs to 50 fs). The resulting ion signal is relatively low because the two photon ionization process is non-resonant and, therefore, inefficient. At a certain time after the excitation by the UV the center of the wavepacket on the first excited state reaches the internuclear separation of 5.73 Å. Here nearly 80% of the wavepacket can be resonantly transferred back to the ground state X by one VIS photon (see minimum of population in Fig. 2.14 b) at 100 fs). Due to conservation of momentum the depumped wavepacket propagates towards larger internuclear separations. About 30 fs after the depumping, a second production channel for Cs$^+$ ions occurs. The depumped
wavepacket is resonantly excited via two VIS photons to the second excited state B and from there ionized by a third VIS photon to the continuum C (see maximum population in Fig. 2.14 d) at 135 fs). This process is extremely effective due to the resonant two photon absorption at internuclear distance 6.18 Å and due to the slowing down of the wavepacket which stops at the turning point at 6.65 Å. These circumstances lead to the maximum ion signal measured at \((150 \pm 15)\) fs shown in Fig. 2.12. In order to support this model the ion signal as a function of the VIS intensity at a delay of 135 fs was measured. The experimental data and the results of the simulations (again rescaled to fit the measurements) are shown in Fig. 2.12b). A good agreement was found.

Increasing the time delay above 150 fs the second channel becomes ineffective because no resonant depumping can occur and so the ion signal drops to a low constant value. The efficiency of the ionization by the VIS pulse, could be directly estimated from the photoionisation cross-section of the Cs atom for large delay times (see appendix 5.1) and a ratio of about 0.26 between the asymptotic populations in the continuum and in state A was obtained in good agreement with the simulations.

Figure 2.15: Time evolution of the population on the different states. The delay time is 150 fs, the pulse parameter are the same as for Fig. 2.12 and 2.16 The curve C on subfigure (c) depicts the sum of the populations on continua \(C^+\) and \(C^-\).
To get a further insight into the process which resulted in the peak of the ion signal, the time evolution of the populations in the different states corresponding to 150 fs delay time is presented in Fig. 2.15. As expected, the states $A^+$ and $B^-$ play negligible roles in the dynamics as indicated by their low populations in Fig. 2.15b). The wavepacket dynamics on the rest of the states are also shown in Fig. 2.16. Although the wavepackets seem to be extremely broad due to the logarithmic gray-scale, the processes can be well recognized when considering that the 186 fs long UV pulse was centered at 300 fs and the 86 fs VIS pulse was centered at 450 fs. The depumping of the wavepacket from state $A^-$ (Fig. 2.16b) to the ground state $X$ (Fig. 2.16a) at internuclear separation of 5.75 Å is clearly seen just as the coherent oscillation of the depumped wavepacket in the ground state. Investigating the wavepacket on state $B^+$ we can see that it is the superposition of two different processes. The first one is a non-resonant temporary population transfer from state $A^-$ by the VIS pulse during the direct two-photon ionization of the molecule from $A^-$. (This results in the elongated ellipse within the spatial and temporal ranges of about (3.5 Å, 9.5 Å) and (350 fs, 500 fs), respectively.) The second process is the repumping of the depumped wavepacket from state $X$ to $B^+$ by two VIS photons. Since this process is resonant at the internuclear distance 6.18 Å, it puts net population to state $B^+$, which is then propagating towards larger internuclear distances. The speed of this wavepacket is clearly slower than that of the wavepacket on $A^-$, due to the fact, that the portion of the wavepacket depumped to $X$ at 5.75 Å lost kinetic energy before it was pumped up to $B^+$ at 6.18 Å. Since the $A\rightarrow X$ transition at around 5.8 Å plays a crucial role in the dynamics, it is worth mentioning, that with the present VIS intensity, this transition is in saturation. Consequently a moderate decrease of $|\mu_{01}|$ within the internuclear distance range of interest, would not alter the computed pump-probe signal considerably. However, the good agreement between the measured and the simulated pump-probe signals verify the usage of a constant $\mu_{01}$.

In order to check the validity of the assumption, that the effect of the uniform original orientation-distribution of the molecules on the pump-probe signal can be neglected, the delay curve shown in Fig. 2.12 (and 2.14(d)) was also computed using half of the intensities.

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9The appearing of the population on state $B^-$ is due to repumping a small portion of the depumped wavepacket from ground state $X$ by the tail of the long UV pulse at internuclear distance 6.18 Å.

10In ref. [24] it was supposed that the $|\mu_{01}|$ may decrease about 20-30% between internuclear distances 2.9 and 5.8 Å. Simulations with smaller $|\mu_{01}|$ values have shown that even if this assumption was true, the clear peak in the pump-probe signal would be still present at the optimum delay. For example, a 20% decrease of $|\mu_{01}|$ results in a peak in the simulated Cs$^+$ signal, which is less than 20% lower than the original one, and thus it is still in satisfactory agreement with the measured data.
Figure 2.16: The figures a) to d) show the wavepacket dynamics on potential surfaces X, A−, B+ and on the first coefficient of continuum C−, respectively. More specifically the quantities $|\Psi^+_0(Q,t)|^2$, $|\Psi^-_1(Q,t)|^2$, $|\Psi^+_2(Q,t)|^2$ and $|\Phi^-_1(Q,t)|^2$ are presented. Transitions among these states are mainly responsible for producing the Cs+ signal, shown in Fig. 2.12. The laser pulse parameters are the same as for Fig. 2.12. The UV and VIS pulses are centered at 300 fs and 450 fs, respectively. The gray-scale is logarithmic, and the darkest color is used above half of the maximum $|\Psi^+/-(Q,t)|^2$ value in each figure.
Figure 2.17: Results of simulation with different intensities. The measured data and the solid curve are the same as in Fig. 2.12. The dashed curve belongs to simulations with reduced pulse intensities. While the pulse width are the same as before, i.e., 186 fs for the UV and 86 fs for the VIS pulse, the intensity of the UV and VIS pulses are now $0.225\, \text{TW/cm}^2$ and $2.35\, \text{TW/cm}^2$, respectively. The original numerical results were rescaled by a factor of 3.8 and 13.4 for the solid and dashed curves, respectively.

for both the UV and the VIS pulses than used in case of Fig. 2.14. This effective intensity corresponds to a relative angle of $45^0$ between the directions of the polarization of the pulses and that of the transition dipole moment vector. The resulting simulated signal is shown in Fig. 2.17 together with the previous simulated and experimental signals. The solid curve corresponds to numerical results with the original intensities while the dashed curve depicts the numerical results with the reduced intensities. For both curves the simulated Cs$^+$ signal (i.e. the population of the ionization continua) was rescaled to fit the measured Cs$^+$ signal. While the scaling factor for the original intensities was 3.8, the results of the simulations with the reduced intensities had to be multiplied by a factor of 13.4 in order to have the same asymptotic value for both curves. As is seen in the figure the two curves have very similar shapes with only a delay of about 40 fs. In order to explain the differences between the two delay curves one has to consider the following.

The amount of population transfered to state A by the UV pulse is similar for both simulations due to the saturation of the X-A transition. The difference in the magnitude of the signals (asymptotic continuum populations) is thus mainly due to the different VIS intensities. There are, however, two effects of the lower UV intensity. First the wavepacket on state A will be broader and second it will escape from the Frank-Condon-region later than in case of the original UV intensity. This delay of the wavepacket is then reflected in

\footnote{It should be notified again, that the polarization of the UV and that of the VIS pulses were the same during the pump-probe experiments.}
the shift of the curve towards larger delay times. Nevertheless, both curves overlap with
the measured data within the uncertainty of the measurement. This fact indicates that
an averaging over the orientations of the molecules would not effect the numerical results
considerably with respect to the experimental data.

The above agreement between numerical and experimental results indicates, that the
dissociation of CsCl was effectively stopped by the depumping process at a time delay of
about 100 fs, 50 fs before the maximum Cs\(^+\) ion signal occurs. Thus using the delay time
as a control parameter according to the Tannor-Rice scheme the portion of dissociating
CsCl molecules can be controlled. An optimal control experiment was then performed
[23, 24, 25] and is reported in the following.

### 2.4.3 Feedback controlled dissociation

A computer running an optimizing self-learning algorithm was implemented to the laser
system in order to vary special laser pulse parameters. Without having any information
upon the CsCl molecule the algorithm had to find the optimal laser pulse parameters for
interrupting the dissociation of CsCl. In order to implement the optimizing algorithms
two more control parameters in addition to the delay were introduced: the prism distance,
and the position of the focusing lens. The prism distance changed the pulse lengths and
the phases of both laser pulses, whereas, positioning of the lens ensured an optimal overlap
between the laser pulse foci and the molecular beam. All three parameters were varied by
stepper motors controlled by the computer running the algorithm. As a feedback signal
the Cs\(^+\) ion signal was used. In the wavepacket simulations it was found (see Fig. 2.14)
that the maximum ion signal occurs about 50 fs after the time delay where the wavepacket
is most efficiently transferred back from state A to the ground state. At the position of the
maximum ion signal the transfer is only about 10% less effective. Therefore, and because
the ion signal is easily accessible it was chosen as an appropriate feedback signal.

The evolution of the three control parameters in case of using a Simulated Annealing
algorithm[77] for optimization is plotted versus the number of iterations in the Figs.
2.18a) to c). The final parameters found are: lens position 5.83 mm, prism distance 68.0 cm
(497 nm: FWHM 190 fs, linear chirp 7 \( \cdot 10^{-5} \) fs\(^{-2}\); 248 nm: FWHM 190 fs, linear chirp
8 \( \cdot 10^{-6} \) fs\(^{-2}\)) and delay 6.794 mm. The Cs\(^+\) ion signal shown in Fig. 2.18d) increases
dramatically with the number of iterations. For randomly chosen parameters the ion signal
is below the detection limit of 100 mV. For the optimized parameters the ion signal
was about 4.0 V which corresponds to an increase of the signal by a factor of 40. The
delay position differed from that in the optimization of the crosscorrelation in propane by \((0.023 \pm 0.001)\) mm. This corresponds to a time delay of \((155 \pm 7)\) fs which in turn is an excellent agreement with the numerical simulations. The final prism distance corresponds again to the maximum intensity of the UV pulse.

The self-learning algorithm, namely the SA algorithm, was able to interrupt the dissociation of CsCl by optimizing the Cs\(^+\) ion signal as a feedback signal. The optimal parameters found by the algorithm, especially the time delay, agrees very well with the parameters obtained in former experiments and in the numerical simulations. Due to the large percentage of transferred populations (> 10%) the present control of the wavepacket motion was clearly in the strong response regime. Thus it was demonstrated for the first time in the strong response regime that a feedback-controlled self-learning system is able to control the dissociation process by optimizing a feedback signal, in this case the ion yield.
Chapter 3

Ab initio and dynamical studies of CH$_2$BrCl dissociation

3.1 Overview

In the present chapter the absorption properties and photodissociation dynamics of the CH$_2$BrCl molecule, a prototype of the multihalomethanes of CH$_2$XY type is investigated. While monohalomethanes (CH$_3$X) have been extensively studied from both experimental [78, 79] and theoretical point of view [80, 81] and thus their photodissociation dynamics are well understood, multihalomethanes have more complicated UV absorption spectra and a greater complexity in the dissociation pathways than their well-studied monohalomethanes analogues. Nevertheless the general features of the dynamics of monohalomethanes served as a reference to understand the more complicated multihalomethanes. For instance, the absorption profile and dynamic properties of CH$_3$Br have been used to deduce those of CH$_2$BrCl [31, 78, 79, 82]. Thus, the absorption peak at 203 nm assigned to the n(Br) $\rightarrow$ $\sigma^*$ (C-Br) transition in CH$_3$Br has been predicted to occur at the same wavelength in CH$_2$BrCl [82]. In agreement to this prediction, UV absorption cross-sections of CH$_2$BrCl have been measured recently finding a maximum at 202.6 $\pm$ 0.5 nm [27]. Unfortunately, no absorption spectrum below 180 nm is yet reported, therefore the absorption peak due to n(Cl) $\rightarrow$ $\sigma^*$(C-Cl) could only be estimated near 164 nm by comparison of that of CF$_2$BrCl, which shows an absorption peak at this wavelength. [83]

Since early investigations, the photolysis of the two bonds C-Br and C-Cl in CH$_2$BrCl have been suggested to be possible, although the C-Cl breaking only around wavelengths of ca. 200 nm [34]. Later investigations using translational spectroscopy have shown that
at 248 nm \( \text{CH}_2\text{BrCl} \) undergoes exclusively C-Br dissociation, while at 193 nm both C-Br and C-Cl fragmentations has been detected with a branching ratio of 4.5 in favor of C-Br against C-Cl fission [28]. A more detailed state-resolved ion time-of-flight mass spectroscopy has been reported in the range 248-268 nm indicating only elimination of the bromine atom, [30] while between 193-242 nm one finds a contribution from the \( \text{n(Cl)} \rightarrow \sigma^*(\text{C-Cl}) \) transition [31]. Furthermore, to verify the character of the ground and excited state halogen atoms and separate the possible influence of the other chromophore, the photodissociation dynamics of \( \text{CH}_2\text{BrCl} \) has been studied at 234 nm using molecular beam-imaging and again C-Br bond cleavage was the only one observed [32].

In the control experiment on \( \text{CH}_2\text{BrCl} \) performed recently by Damrauer et. al. [10] a phase-shaped femtosecond laser pulse of wavelength of 800 nm has been applied to maximize the ratio of the photoproduct ions, i.e., \( \text{CH}_2\text{Br}^+ / \text{CH}_2\text{Cl}^+ \), detected by a mass-spectrometer. The pulse shape was optimized according to the scheme proposed by Judson and Rabitz [14] (see chapter 1). As a result a \( \text{CH}_2\text{Br}^+ / \text{CH}_2\text{Cl}^+ \) ratio of 1:6 was achieved, which is a factor 2 improvement with respect to reference value obtained by the original transform limited pulse. From the weak intensity dependence of the relative yield of the parent ion, the authors assumed that the fragmentation did not take place in an ionic surface. Instead it was assumed, that the transform limited 800 nm pulse excited the molecule to a Rydberg state from which they were predissociated by an ion-pair state. The shaped pulse optimizing the product ion ratio has lower intensity, so it was assumed that the control was achieved on the lower lying \( \text{n(X)} \rightarrow \sigma^*(\text{C-X}) \) surfaces (X=Br,Cl). Differences of the Br\(^+\) and Cl\(^+\) yields between the mass spectra obtained with and without the optimization seemed to support this assumption. Nevertheless neither a direct evidence for these suppositions nor any conclusion from the optimized pulse shape concerning the actual control mechanism could be presented.

The only available numerical study of the photodissociation dynamics of \( \text{CH}_2\text{BrCl} \), based on model potentials, indicated that nonadiabatic dynamics should play an important role in the C-Cl bond fission. [39] The present chapter reports about the first high level \textit{ab initio} results of transitions to the low-lying singlet states of \( \text{CH}_2\text{BrCl} \) through multiconfigurational calculations. [84, 85] One dimensional potential energy- and corresponding transition dipole moment curves for the lowest three singlet electronic states of symmetry \( \text{A'} \) are presented. The nonadiabatic dynamics is then investigated by preliminary one dimensional wavepacket propagations on the basis of these high accuracy \textit{ab initio} results. [85] Finally, a Tannor-Rice control scheme based on the properties of the potential energy- and TDM-curves will be suggested as an alternative way of achieving
bond-selective dissociation of CH\textsubscript{2}BrCl in favor of the stronger C–Cl bond with respect to the weaker C–Br one in the neutral dissociation channel.

\section{3.2 Theoretical background}

\subsection{3.2.1 The CASSCF and MS-CASPT2 methods}

In order to obtain the potential energy surfaces and transition dipole moments that are necessary for the simulation of the photodissociation process, Eq. 1.5 has to be solved for the electronic wavefunctions $\Phi_j(R, r)$ and the energies $V^a_j(R)$. An exact solution is not possible for any but the most simple molecular systems. Thus, approximations are needed. The first of the most common approximations is to build the wavefunction from molecular orbitals. Since the electron wavefunction should be antisymmetric, the simplest solution is the Slater-determinant, which is made of $n/2$ orbitals for a molecule containing $n$ electrons:

$$D_0 = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(r_1) \alpha(1) & \phi_1(r_1) \beta(1) & \cdots & \phi_{n/2}(r_1) \beta(1) \\ \phi_1(r_2) \alpha(2) & \phi_1(r_2) \beta(2) & \cdots & \phi_{n/2}(r_2) \beta(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(r_n) \alpha(n) & \phi_1(r_n) \beta(n) & \cdots & \phi_{n/2}(r_n) \beta(n) \end{vmatrix}$$

(3.1)

Here $\alpha$ and $\beta$ are the two spin-functions and the variables $r_i$ are the coordinates of the individual electrons $i$. The molecular orbitals $\phi_j(r)$ are linear combinations

$$\phi_j(r) = \sum_k c_{jk} \varphi_k(r)$$

(3.2)

of the so called contracted basis functions, $\varphi_k(r)$, representing atomic orbitals, which are themselves predefined as linear combinations of some primitive basis functions like gaussian-type atomic functions.

The problem now is to find the molecular orbital expansion coefficients, $c_{jk}$. This is usually done on the basis of the variational principle, which states that for any antisymmetric normalized function of the electronic coordinates the corresponding expectation value of the energy is always greater or equal than the energy of the exact wavefunction. Hence, the problem reduces to minimize the energy of the wavefunction by optimizing the coefficients subject to the constraint that the wavefunctions are orthonormal. The variational principle leads to equations which are nonlinear for the coefficients and therefore they have to be solved iteratively. (The resulting equations for the electronic ground state are the
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Roothaan-Hall equations. [86]) This iterative procedure is called the self-consistent-field (SCF) procedure and it is the essence of the Hartree-Fock (HF) method. In this procedure only one Slater determinant is considered. Although the so-called exchange correlation is automatically included in this method by antisymmetrizing the wavefunction, the shortcoming of this treatment is that each electron sees all of the other electrons as an average distribution and then no instantaneous electron-electron interaction is included, i.e., the so-called dynamical correlation is missing. One way to recover the electronic correlation is to use perturbation theory (PT). Second order perturbation based on the single Hartree-Fock determinant as a reference wavefunction (Moller-Plesset (MP2) perturbation theory [87]) is usually enough to account for 85-90% of dynamical correlations and therefore, results in reliable ground state energies and optimized geometries. However, due to the usage of a single determinant as a reference function, the asymptotic behaviour of this method for dissociating systems is uncorrect, i.e., the so-called statical correlation is missing. In that cases, the only way to overcome this problem and at the same time recover the dynamical correlation is to use the configuration interaction (CI) method.

In the CI procedure the wavefunction is constructed as a linear combination of several determinants (including the original HF-determinant) each of which is generated from the original HF determinant, \( D_0 \), by substituting one or more occupied molecular orbitals (\( \phi_a, \phi_b, \ldots \)) with virtual (unoccupied) ones (\( \phi_r, \phi_s, \ldots \)) as

\[
\Theta_p = C_{p,0} D_0 + \sum_{r,a} C_{p,a}^r D_a^r + \sum_{a<b} \sum_{r<s} C_{p,ab}^{rs} D_{ab}^{rs} + \cdots \tag{3.3}
\]

where \( D_a^r, D_{ab}^{rs}, \ldots \) denote determinants with single-, double-, ... substitutions, respectively. The coefficients \( \{ C_{p,0}, C_{p,a}^r, C_{p,ab}^{rs}, \ldots \} \) are called configuration interaction (CI) coefficients. The CI is full if the summation runs over all occupied and virtual orbitals and all the possible substitutions (single-, double-, ...) are included in the expansion. The full CI (FCI) results in the best wavefunction that can be constructed within a given basis set. It accounts for the dynamical correlations and shows a good asymptotic behavior for dissociating systems. Indeed, if the basis set is complete, the FCI is exact. However, the number of molecular orbitals is usually too large to perform a FCI, so either the number of possible substitutions is restricted to single or double substitutions (CIS, CID, CISD methods) or substitutions are restricted within a certain subspace of the whole configuration space, i.e., to a certain group of molecular orbitals where FCI is performed. In the first case the truncated CI is not size-consistent \(^1\) while in the second case a large amount of the dynamical correlation is lost. Although dynamical correlation, in principle, could be

\(^1\) Considering a "supermolecule" composed of two noninteracting parts (separated by a large distance)
recovered in a subsequent PT2 computation, the fact that the substituted determinants come from one initial configuration, i.e., from the previously determined Hartree-Fock determinant, $D_0$, do not always provide a good zeroth order reference function for the PT2 treatment (e.g. in the case of excited states). In that case more than one configuration (determinant) as a starting wavefunction is needed, leading to the so-called multiconfigurational self-consistent field (MCSCF) methods. In this procedure both the molecular orbital expansion coefficients and the CI coefficients are optimized simultaneously. One of such MCSCF methods is the complete active space self-consistent field method (CAS or CASSCF). [88]

In case of the CAS method the molecular orbitals are categorized into three groups according to their energies: inactive, active and secondary orbitals (see Fig. 3.1). The inactive orbitals are those that are always doubly occupied and do not change during the chemical reaction; likewise, the secondary orbitals do not intervene either and are always empty. Only the active orbitals are allowed to have partial occupation numbers, they constitute the active space and within this active space the CI is full.

Figure 3.1: Schematic representation of dividing the orbital space into inactive, active and secondary spaces in case of the complete active space (CAS) method. Within the active space all possible substitutions are allowed. (In the figure only a single substitution is indicated).

In the present work the CASSCF method together with a subsequent multistate PT2 treatment was used to compute the potential energy surfaces and transition properties for the CH$_2$BrCl molecule. The first step towards this level of computation is to compute the
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CASSCF wavefunction for the ground state of the molecule starting from the Hartree-Fock determinant. In order to compute the electronic excited states, a state-averaged CASSCF (SA-CASSCF) calculation is performed for a given symmetry and spin. This means, that one does not optimize the ground state alone but simultaneously all the electronic states of interest in an averaged way, by minimizing the weighted sum of their energies, where the weights express the ‘importance of the states’. (In all of our computations the states were weighted equally.) As a result, one gets the CASSCF wavefunctions, $\Theta^\text{CASSCF}_p$ and their corresponding energies, $E^\text{CASSCF}_p$ for each electronic state. To account for the dynamical correlation, these wave functions were used in a subsequent Multi-State second order perturbation (MS-CASPT2) treatment [89]. The MS-CASPT2 approach uses a multi-dimensional reference space by coupling simultaneously different single state CASPT2 (CASPT2 or SS-CASPT2) states [90] of the same symmetry previously included in the SA-CASSCF wave function. That is, first, a perturbation computation (SS-CASPT2) is performed separately for each electronic state. For these computations the Hamiltonian $\hat{H}^{el}(R, r)$ (see Eq. 1.2) is partitioned into a zeroth-ordered part $H_0$, constructed by the one-particle Fock-operators $^2$ and a perturbation term $V$ containing the two-particle correlation terms. Although the total Hamiltonian, $\hat{H}^{el}(R, r)$ (denoted further as $H$) is of course unique, and the final wavefunctions are all eigenfunctions of this Hamiltonian, the partitioning is done separately for each electronic state $i$ as

$$H = H_0^i + V^i$$

and for each SS-CASPT2 computation the corresponding SA-CASSCF wavefunction $\Theta^\text{CASSCF}_i$ is used as the reference (zeroth-order) wavefunction. As a result, one obtains the second-order SS-CASPT2 energies and first-order SS-CASPT2 wavefunctions. The SS-CASPT2 solution $\Theta^\text{CASPT2}_i$ for the electronic state $i$ is coming from the CASSCF wavefunction $\Theta^\text{CASSCF}_i$ as:

$$\Theta^\text{CASPT2}_i = \Theta^\text{CASSCF}_i + \Theta^\text{pert}_i$$

where $\Theta^\text{pert}_i$ is the first-order perturbation correction to the CASSCF reference wavefunction forced to be orthogonal to the reference space wavefunctions. The second-order perturbation corrections to the energy, $e_{ij}$, can be computed as

$$e_{ij} = \langle \Theta^\text{CASSCF}_i | V | \Theta^\text{pert}_j \rangle$$

$^2$The Fock-operator for the electron $i$ is $\hat{F}_i = \hat{h}_i + \sum_j (\hat{J}_j - \hat{K}_j)$. Here, $\hat{h}_i$ describes the kinetic energy of the electron $i$ and its attraction to all the nuclei. $\hat{J}$ and $\hat{K}$ are, respectively, the Coulomb- and exchange operators, describing the repulsion of the electron to all the other electrons.
This correction is the CASPT2 correlation energy. The total SS-CASPT2 energy for electronic state $i$ is the sum of $E_i^{\text{CASSCF}} + e_{ii}$, where $E_i^{\text{CASSCF}}$ is the CASSCF energy for state $i$ given by

$$\langle \Theta_i^{\text{CASSCF}} | H | \Theta_j^{\text{CASSCF}} \rangle = \delta_{ij} E_i^{\text{CASSCF}} \quad (3.7)$$

For some systems, (e.g. benzene and azabenzenes [91, 92]), the SS-CASPT2 energies are already good approximations to the exact solution. However, the SS-CASPT2 method can be inadequate at avoided crossings. The MS-CASPT2 method on the other hand, has been shown to be able to describe near degeneracies correctly. The SS-CASPT2 results can also be incorrect when erroneous valence-Rydberg mixing occurs at the CASSCF level, such as in the case of the excited states of ethene, butadiene or n-tetrasilane [89, 93, 94]. In all of these cases the MS-CASPT2 method was able to separate effectively the computed states which could be then clearly identified as either valence or Rydberg states. Since our model system, CBM, presents Rydberg states as well as several degeneracies, MS-CASPT2 has been applied in the present work.

In this extension of SS-CASPT2 a symmetric effective Hamiltonian, $H^{\text{eff}}$, is constructed as

$$H^{\text{eff}}_{ij} = E_i^{\text{CASSCF}} \delta_{ij} + \frac{1}{2} (e_{ij} + e_{ji}) , \quad (3.8)$$

where the diagonal terms are the SS-CASPT2 energies and the off-diagonal terms are the couplings between the CASSCF states $i$ and $j$ via the dynamical correlation. In this way all states of a given symmetry can be simultaneously treated including a high degree of correlation effects. Diagonalizing this effective Hamiltonian matrix results in the final MS-CASPT2 energies. The final MS-CASPT2 wavefunction, $\Theta_i^{\text{MS-CASPT2}}$, for the electronic state $i$ can be also written as

$$\Theta_i^{\text{MS-CASPT2}} = \Theta_i^{\text{PMCAS}} + \Theta_i^{\text{pert}} , \quad (3.9)$$

where $\Theta_i^{\text{PMCAS}}$ is called "Perturbation Modified CAS" (PMCAS) wavefunction and it is simply a linear combination of the CASSCF reference functions:

$$\Theta_i^{\text{PMCAS}} = \sum_q \hat{C}_{iq} \Theta_q^{\text{CASSCF}} . \quad (3.10)$$

These $\Theta_i^{\text{PMCAS}}$ states are used to compute the transition dipole moments according to Eq. 1.11 as well as other properties as e.g. the expectation values of the cartesian moments.


3.2.2 Laser-induced wavepacket propagations

In the previous section we have discussed the ab initio methods that were applied to solve the TISE (Eq. 1.5) for the electronic wavefunctions \( \Theta_i(Q, r) \) and potential energies \( V^a_{ii}(Q) \). Now we turn back again to the TDSE, expressed in the adiabatic representation by Eqs. 1.6 and 1.10 for the nuclear wavefunctions \( \Psi^a_i(Q, t) \).

As long as non-adiabatic couplings between the electronic states are not considered, the following form of the Schrödinger equation governs the dynamics in one dimension (\( Q \)):

\[
\frac{i\hbar}{\partial t} \Psi^a_i(Q, t) = \left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial Q^2} + V^a_{ii}(Q) \right] \Psi^a_i(Q, t) - \sum_j \varepsilon(t) D_{ij}(Q) \Psi^a_j(Q, t) \tag{3.11}
\]

where \( m \) is the reduced mass of the molecule corresponding to one carbon-halogen bond stretching and \( \Psi^a_i(Q, t) \) is the nuclear wavefunction belonging to the adiabatic state \( i \). Unlike the previous computations for the CsCl molecule, in the present case the effect of the molecular orientation with respect to the laser-polarization is explicitly taken into consideration by introducing the rotational matrix, \( D \) into the laser coupling term on the r.h.s of the Eq. 3.11. The \( D \) matrix transforms the laboratory-fixed coordinates of the electric field vector, \( \varepsilon(t) \) into the molecule-fixed ones. The electric field vector, \( \varepsilon(t) \), has the general form

\[
\varepsilon(t) = E_0(t) \cos(\omega_0 t) S(t) \tag{3.12}
\]

where \( \omega_0 \) is the central frequency of the laser pulse, \( E_0 \) is the peak amplitude of the electric field and the envelope \( S(t) \) will have a sine square shape in the forthcoming simulations:

\[
S(t) = \begin{cases} 
\sin^2 \frac{\pi}{2T} \left( 2 \left( t - t_0 \right) + T \right) & \text{if } t_0 - \frac{T}{2} \leq t \leq t_0 + \frac{T}{2} \\
0 & \text{otherwise}
\end{cases} \tag{3.13}
\]

with time duration \( T \) (corresponding to a FWHM of 0.364 \( T \) in intensity) and a peak amplitude centered at time \( t_0 \).

In order to describe the population dynamics at around an avoided crossing in the adiabatic representation, the kinetic coupling (Eq. 1.8) should be kept in the TDSE (Eq. 1.6). However, working in the adiabatic representation, i.e., with kinetic couplings, may be for two reasons not advantageous: i) the first-order kinetic coupling term (Eq. 1.7) contains derivations of the nuclear wavefunction which can not be easily implemented in the efficient and reliable SPO method and ii) the \( T_{ij}^{(2)} \) kinetic coupling element is often sharply peaked or even singular when the wavefunction changes rapidly within a narrow space, which can cause numerical problems in simulating the wavepacket-motion through an
avoided crossing in the adiabatic representation. Nevertheless, in a physically equivalent representation, i.e., the so called diabatic representation, these problems can be avoided since the kinetic couplings are forced to vanish and a potential-like coupling appears instead, which is numerically easier to handle. The nuclear wavefunctions $\Psi_d^j(Q, t)$ in the diabatic representation are interconnected with the adiabatic ones, $\Psi_a^j(Q, t)$ by

$$
\Psi_d^j(Q, t) = \sum_k U^+_{jk} \Psi_a^k(Q, t),
$$

where the unitary transformation matrix $U$ was shown to fulfill the differential equation

$$
\frac{\partial}{\partial Q} U = -T^{(1)} U.
$$

Here, $T^{(1)}$ is the first-order kinetic coupling term (Eq. 1.8a). The diabatic potential matrix $V^d$ as well as the diabatic TDM matrix, $\mu^d$ can be obtained from their adiabatic pairs $V^a$ and $\mu^a$ with the help of the unitary transformations

$$
V^d = U^+ V^a U, \quad \mu^d = U^+ \mu^a U.
$$

The Schrödinger equation in the diabatic representation is then:

$$
i\hbar \frac{\partial \Psi^d_i(Q, t)}{\partial t} = \left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial Q^2} + V^d_{ii}(Q) \right] \Psi^d_i(Q, t) + \sum_{j \neq i} \left[ V^d_{ij}(Q) - \xi(t) \mu^d_{ij}(Q) \right] \Psi^d_j(Q, t).
$$

In principle, $T$ could be numerically evaluated directly from the ab initio wavefunctions $\Theta_j^a(Q, r)$ (see Eq. 1.8). In practice, this requires the differentiation of the wavefunction, which then has to be evaluated as a function of the internuclear distance with a very high resolution. Instead the diabatization procedure described in ref. [96] is applied in the present work, i.e., the kinetic coupling matrix $T$ is approximated with the help of an asymmetric Lorentzian function given by:

$$
T_{ij} = \left\{ \begin{array}{ll}
\frac{2\Gamma^l_{ij}}{4(Q-r^c_{ij})^2+(\Gamma^l_{ij})^2} & \text{for } Q \leq r^c_{ij} \\
\frac{2\Gamma^r_{ij}}{4(Q-r^c_{ij})^2+(\Gamma^r_{ij})^2} & \text{for } Q > r^c_{ij}
\end{array} \right.
$$

where $r^c_{ij}$ stands for the location of the crossing and $\Gamma^l_{ij}$ and $\Gamma^r_{ij}$ determine the half-widths of $T_{ij}(Q)$ from the left and right hand side of the crossing, respectively.
3.2.3 Evaluation of population dynamics

In order to evaluate the results of the wavepacket simulations an expression for the probability of dissociation as well as for dissociation time, equally valid for both representations are needed. Such expressions can be introduced similarly to ref. [97]. First we assume that the laser pulse is linearly polarized in a single direction, i.e., in the $y$ direction in the laboratory-fixed coordinate system. Let $D_{yq}$ denote the element of the rotational matrix transforming the $q$ component of the transition dipole moment vector $\mu_{j1}$ in the molecule-fixed coordinate system. Assuming that the molecules do not rotate within the short time interval of the dissociation process, the (nuclear) wavepacket on the excited state $j$ can be expressed for any time $t$, as

$$\Psi_{ij}^{(i)}(Q, t) = D_{yq} \tilde{\Psi}_{jx}^{(i)}(Q, t) + D_{yz} \tilde{\Psi}_{jz}^{(i)}(Q, t)$$  \hspace{1cm} (3.19)

where $\tilde{\Psi}_{jq}^{(i)}(Q, t)$ is the solution of the TDSE in the case where the $q$ component of $\mu_{j1}$ is parallel to the electric field polarization ($y$) and the electric field populates initially the (diabatic or adiabatic) excited state $i$. The population on the excited state $j$ at the time $t$ is then expressed by

$$P_{ij}^{(i)}(t) = \int_{0}^{\infty} |\Psi_{ij}^{(i)}(Q, t)|^2 dQ = \int_{0}^{\infty} |D_{yq} \tilde{\Psi}_{jx}^{(i)}(Q, t) + D_{yz} \tilde{\Psi}_{jz}^{(i)}(Q, t)|^2 dQ$$  \hspace{1cm} (3.20)

In order to take into consideration the uniform distribution of molecule-orientations in the laboratory coordinate system one can perform a classical averaging over the molecular orientations. Using the orientation averages of the rotational matrix elements,

$$D_{yx}^2 = D_{yz}^2 = \frac{1}{3} \text{ and } D_{yx}D_{yz} = 0,$$  \hspace{1cm} (3.21)

the following expression is obtained for the average population $\overline{P_{j}^{(i)}(t)}$ in electronic state $j$:

$$\overline{P_{j}^{(i)}(t)} = \overline{P_{jx}^{(i)}(t) + P_{jz}^{(i)}(t)},$$  \hspace{1cm} (3.22)

where

$$\overline{P_{jq}^{(i)}(t)} = \frac{1}{3} \int_{0}^{\infty} |\tilde{\Psi}_{jq}^{(i)}(Q, t)|^2 dQ.$$  \hspace{1cm} (3.23)

The total excited population $\overline{P^{(i)}}$ is of course constant after the pulse has ceased ($t > T/2 + t_0$) and it is the sum of the population in the first ($j=2$) and in the second ($j=3$) excited states

$$\overline{P^{(i)}} = \overline{P_2^{(i)}(t)} + \overline{P_3^{(i)}(t)}.$$

(3.24)
The probability of dissociation, \( P_{\text{diss}} \), can be computed similar to the populations (Eqs. 3.20-3.24) by changing the lower limit (0) of integration over \( R \) to the boundary \( b \), between the interaction \((Q < b)\) and asymptotic \((Q > b)\) domains of the potentials. In other words, the probability of dissociation is given by that portion of the wavepacket, which is out of the limit \( b \). Thus, the time-dependent probability of dissociating a molecule is

\[
P_{\text{diss},i}^{(i)}(t) = P_{\text{diss},2}^{(i)}(t) + P_{\text{diss},3}^{(i)}(t) ,
\]

where \( P_{\text{diss},j}^{(i)}(t) \) is

\[
P_{\text{diss},j}^{(i)}(t) = \int_{b}^{\infty} |\tilde{\Psi}_{jQ}^{(i)}(Q, t)|^2 dQ = \int_{b}^{\infty} |D_{yj} \tilde{\Psi}_{jx}^{(i)}(Q, t) + D_{zj} \tilde{\Psi}_{jz}^{(i)}(Q, t)|^2 dQ ,
\]

i.e., the probability of dissociating the molecule in the excited state \( j \), in case of initially populating its excited state \( i \) by the laser pulse. Performing again the classical averaging over the molecule-orientations one gets

\[
\overline{P}_{\text{diss},j}^{(i)}(t) = \overline{P}_{\text{diss},jx}^{(i)}(t) + \overline{P}_{\text{diss},jz}^{(i)}(t) ,
\]

where

\[
\overline{P}_{\text{diss},jq}^{(i)}(t) = \frac{1}{3} \int_{b}^{\infty} |\tilde{\Psi}_{jq}^{(i)}(Q, t)|^2 dQ .
\]

Since we are not interested in the probability of dissociating of all the molecules\(^3\) but of those, that were already excited by the pulse, we should normalize the \( \overline{P}_{\text{diss}}^{(i)} \) by the population of the excited states, \( \overline{P}_{\text{diss}} \) after the pulse.

If the dissociation takes place in one step, the corresponding \( \overline{P}_{\text{diss}}(t) \) curves (both diabatic and adiabatic ones) can be usually very well fitted by the following sigmoid function

\[
\overline{P}_{\text{diss}}(t) = \overline{P}_{\text{diss}} \left[ 1 + e^{-\left(t - t_{\text{diss}}'\right) / Dt} \right]^{-1} ,
\]

where the parameter \( Dt \) is determined by the length of the pulse, \( \overline{P}_{\text{diss}} \) is the asymptotic dissociation probability and \( t_{\text{diss}}' \) is the time at which \( \overline{P}_{\text{diss}}(t) \) takes the half of its maximum value \( \overline{P}_{\text{diss}} \). This moment can be taken as the ‘absolute’ time of the dissociation. In case of a pulse with energy density far below the saturation energy density centered at time \( t_0 \), the dissociation time \( t_{\text{diss}} \) can be defined as

\[
t_{\text{diss}} = t_{\text{diss}}' - t_0 .
\]

\(^3\)This probability is much less than 1 due to the assumption that the excitation is in the perturbative regime.
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To get a first insight into the dissociation dynamics and to determine the dissociation times, it is enough to assume, that the system is excited by a pulse whose duration is sufficiently short compared to the timescale of the non-adiabatic dynamics but its bandwidth is still narrow enough to populate either one or the other excited state. We will call such a pulse quasi-δ-pulse and its duration will be denoted by δt. In case of populating the excited state $i$ by the quasi-δ-pulse, an initial condition for the wavepacket dynamics after time $t = δt$ (the duration of the pulse) can be generally written for excited state $j$ as

$$\tilde{\Psi}_{ij}^{(i)}(Q, δt) = \frac{i}{\hbar} δt E_q \mu_{j1q}(Q) \Phi_{0}^{(1)}(Q) \delta_{ij} ,$$ (3.31)

for $q = x$ and $z$, where $Φ_{0}^{(1)}(Q)$ denotes the lowest vibrational eigenfunction of the electronic ground state, denoted by the index $j=1$, in which the molecule is assumed to reside before interacting with the electric field. In case of a real exciting laser pulse with a finite duration, the initial condition should be given at time $t = 0$ fs for the state $j$ as

$$\tilde{\Psi}_{ij}^{(i)}(Q, 0) = Φ_{0}^{(1)}(Q) \delta_{ij} .$$ (3.32)

3.3 Vertical excitations of CH₂BrCl in the equilibrium geometry

3.3.1 Computational details

The equilibrium geometry for the ground state of CH₂BrCl has been determined at the MP2(fc)/6-311+G(d,p) level of theory. The relevant geometrical parameters are shown in Fig. 3.2. Using this optimized geometry the vertical excitation energies for the lowest singlet excited states and their relative transition dipole moments have been calculated using multiconfigurational methods. The calculations have been carried out within the $C_s$ symmetry constraint, with the Br atom placed in the z axis and the Cl in the xz plane (cf. Fig. 3.2).

Generally contracted basis sets of the Atomic Natural Orbital (ANO-L) type were employed for C, H and Cl atoms [99], whereas a relativistic effective core potential (ECP)
CHAPTER 3. AB INITIO STUDY OF CH₂BRCL DISSOCIATION

Figure 3.2: Equilibrium ground state structure of CH₂BrCl optimized at MP2/6-311+G(d,p) level of theory, together with its molecular orientation. The optimized values of C–Br and C–Cl distances as well as that of the Br-C-Cl angle are shown in the figure. Further optimized geometry parameters are C-H=1.086 Å, Br-C-H=107.3°, Cl-C-H=108.8° and H-C-H=111.2°.

approximation was used for the Br atom. Specifically, the following contraction schemes were used: a (14s9p4d) set contracted to [4s3p2d] for the C atom, a (8s4p)/[3s2p] set for the H atoms, a (17s12p5d)/[5s4p2d] set for the Cl atom and the AIMP (9s8p4d)/[3s4p2d] (Z=7.0) ECP [100] for the Br atom. The ANO-L basis sets are designed to treat correlation and polarization effects in an optimal way so they should be large enough to calculate the excitation energies as accurately as possible. To describe correctly not only valence states but also the low-energy Rydberg states the former valence basis sets for C, Cl and Br have been augmented with an extra set of 2s’2p’1d’ diffuse functions constructed from the primitive uncontracted set, with exponents generated following the standard procedure devised by Kaufmann et al. [101]. A total number of 132 basis functions are comprised in the calculations.

In the CASSCF spectrum some valence excited states may be misplaced at considerably high energies. Since the inclusion of dynamical correlation can drastically alter the order of the states when going from CASSCF to SS-CASPT2, it is therefore necessary to include a sufficient number of states in the SA-CASSCF wavefunction to guarantee that no low lying state is missing at the CASPT2 level. Based on a large number of testing calculations we have determined that in order to describe the low energy valence states for the CH₂BrCl and obtain a balanced description of the mixing in the zero order wavefunction, eleven roots of A’ symmetry and ten roots of A” states are to be included. The active space used in the SA-CASSCF calculation contains twelve electrons correlated in twelve orbitals, including the molecular orbitals from 9a’ to 16a’, and from 3a” to 6a”, which correspond to the \( \sigma, \sigma^*(\text{C-Br}), \sigma, \sigma^*(\text{C-Cl}), n_z(\text{Cl}), n_x(\text{Br}), n_y(\text{Cl}), n_y(\text{Br}), \) plus Rydberg orbitals. The a’A’ electronic ground state configuration conforms to a close shell occupation \( (9a')^2 (10a')^2 (11a')^2 (12a')^2 (3a'')^2 (4a'')^2 (13a')^0 (14a')^0 \) corresponding to a \( \sigma(\text{C-Cl})^2 \sigma(\text{C-Br})^2 n_z(\text{Cl})^2 n_x(\text{Br})^2 n_y(\text{Cl})^2 n_y(\text{Br})^2 \sigma^*(\text{C-Cl})^0 \sigma^*(\text{C-Br})^0 \) configuration.

A well-known problem in CASPT2 is the occurrence of intruder states, which is more
critical when a large number of diffuse functions are used in the basis set [102]. The best way to remove intruder states is to increase the active space, such that the intruder state is moved into the CAS CI space. However, in the present case the active space is close to practical limitations, therefore the level shift (LS) technique had to be used [103]. In the level-shift technique a constant energy term is added to the external part of the zeroth-order Hamiltonian in order to avoid a weak singularity due to accidental degeneracy. After a careful analysis it was found that with a value of LS=0.3 au (Hartrees) reliable CASSCF reference weights $\omega$ in the CASPT2 calculation are obtained and the correlated energies are converged.

The CASSCF state interaction method [104] was used to calculate the transition dipole moments $\mu_{ij}$ from the corresponding perturbed-modified CAS (PMCAS) reference function. The oscillator strengths $f_{ij}$ were then calculated as $2/3\mu_{ij}^2\Delta E$ using the energy differences $\Delta E$ obtained at the MS-CASPT2 level.

All the CASSCF/MS-CASPT2 calculations were carried out using the MOLCAS 5.0 quantum chemistry software [105] while MP2 calculations were performed with the GAUSSIAN98 package of programs [106]. These computations were performed on the HP workstations of the Theoretische Chemie group of the Freie Universität Berlin.

### 3.3.2 Results and discussion of ab initio computations

The structure of CH$_2$BrCl optimized at the MP2/6-311+G(d,p) level of theory is shown in Fig. 3.2. There are significant differences with the MP2/6-31G values previously reported in the literature [32] concerning the C-Br and C-Cl distances, which are shortened by ca. 0.1 Å in the present work. No experimental structure is available, but the experimental vibrational frequencies [107] and those calculated with MP2/6-311+G(d,p) and scaled by the empirical factor 0.9646 [108] (See Table 3.1) are in a very good agreement (< 2 % error), validating our molecular structure.

The vertical excitation energies of the singlet valence and Rydberg excited states of A’ symmetry of CH$_2$BrCl obtained by CASSCF and SS-CASPT2 calculations, together with the composition of the wavefunction, and the corresponding oscillator strengths, $f$, are collected in Table 3.2. Since the expectation value of the total second cartesian moments, $R^2$ is always considerably larger for the Rydberg than for the valence states, it can serve to differentiate valence from Rydberg states. Hence, it was also computed and included in the table. The last column in Table 3.2 contains the weight of the reference wavefunction (CASSCF) in the first order perturbed approach. In all cases the values are between
CHAPTER 3. AB INITIO STUDY OF CH₂BRCL DISSOCIATION

<table>
<thead>
<tr>
<th>Type of mode</th>
<th>Exper.(^a)</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br-C-Cl bending</td>
<td>229</td>
<td>230</td>
</tr>
<tr>
<td>C-Br stretching</td>
<td>614</td>
<td>617</td>
</tr>
<tr>
<td>C-Cl stretching</td>
<td>744</td>
<td>764</td>
</tr>
<tr>
<td>CH₂ rocking</td>
<td>852</td>
<td>847</td>
</tr>
<tr>
<td>CH₂ twisting</td>
<td>1128</td>
<td>1144</td>
</tr>
<tr>
<td>CH₂ wagging</td>
<td>1231</td>
<td>1263</td>
</tr>
<tr>
<td>CH₂ bending</td>
<td>1482</td>
<td>1416</td>
</tr>
<tr>
<td>CH₂ s-stretching</td>
<td>3003</td>
<td>3052</td>
</tr>
<tr>
<td>CH₂ a-stretching</td>
<td>3066</td>
<td>3129</td>
</tr>
</tbody>
</table>

Table 3.1: Scaled harmonic vibrational frequencies at the MP2/6-311+G(d,p) level (in cm\(^{-1}\)) compared with the experimental ones and its corresponding assignments.

\(^a\)Taken from Ref. [107]

0.89-0.85 indicating that calculations performed with LS=0.3 au are balanced and most intruder states have been supressed.

At the CASSCF level there is a considerable mixing of valence and Rydberg states in the first five excitations. In Table 3.2, only those configurations with a coefficient higher than 0.4 are reported. Nevertheless a small fraction of a Rydberg transition is also present in the b\(^1\)A’ state, as well as small contributions of valence states are present in the c\(^1\)A’ and d\(^1\)A’ states at CASSCF level, -not shown in the table- indicating a deficient description of the low lying spectrum at this level of theory. The values of R\(^2\) also reflect this valence-Rydberg mixing. The values for the valence states are expected to be close to the ground state value of 73 au, whereas values for the second moments in Rydberg states vary from 120 au to 200 au, depending on the character of the Rydberg state. Those denoted by Rydb A’ correspond mainly to an excitation to the 3s orbital, while the Rydb A” are excitations to different combinations of 3p orbitals.

The inclusion of dynamical correlation by means of SS-CASPT2 alters dramatically the order of the states, dropping considerably in energy the valence states. See for instance, that the valence state n\(_x\)(Br)→\(\sigma^+(C-\text{Cl})\) in k\(^1\)A’ at CASSCF level, appears at SS-CASPT2 level much lower in energy and heavily mixed with other valence states, as n\(_z\)(Cl)→\(\sigma^+(C-\text{Br})\) in e\(^1\)A’ and h\(^1\)A’ roots. However, single root CASPT2 does not remove all the valence-Rydberg mixing, as it can be observed in the states d\(^1\)A’ and g\(^1\)A’. It is therefore to be expected that the energies provided by the SS-CASPT2 are still not reliable. It is also worth noting that the mixing in the wave function also varies substantially in going from CASSCF to SS-CASPT2.
Table 3.2: CASSCF and SS-CASPT2 calculated excitation energies with their corresponding one-electron excitations (weighting coefficients in parenthesis), expectation values of $R^2$, oscillator strengths $f$, and weight of the reference CASSCF function $\omega$, for $A'$ states.

<table>
<thead>
<tr>
<th>Transition</th>
<th>CASSCF</th>
<th></th>
<th></th>
<th>SS-CASPT2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a^1A' \rightarrow b^1A'$</td>
<td>$n_z(\text{Br}) \rightarrow \sigma^*(C - Br)$</td>
<td>(-0.71)</td>
<td>6.92</td>
<td>81.9</td>
</tr>
<tr>
<td></td>
<td>$n_z(\text{Cl}) \rightarrow \sigma^*(C - Br)$</td>
<td>(-0.47)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a^1A' \rightarrow c^1A'$</td>
<td>$n_z(\text{Br}) \rightarrow \text{Rydb.} A'$</td>
<td>(0.66)</td>
<td>7.57</td>
<td>115.7</td>
</tr>
<tr>
<td></td>
<td>$n_z(\text{Cl}) \rightarrow \text{Rydb.} A'$</td>
<td>(-0.60)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a^1A' \rightarrow d^1A'$</td>
<td>$n_y(\text{Br}) \rightarrow \text{Rydb.} A''(2)$</td>
<td>(-0.54)</td>
<td>8.13</td>
<td>140.9</td>
</tr>
<tr>
<td></td>
<td>$n_y(\text{Cl}) \rightarrow \text{Rydb.} A''(1)$</td>
<td>(0.51)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a^1A' \rightarrow e^1A'$</td>
<td>$n_z(\text{Br}) \rightarrow \text{Rydb.} A''(1)$</td>
<td>(-0.48)</td>
<td>8.29</td>
<td>108.3</td>
</tr>
<tr>
<td></td>
<td>$n_z(\text{Cl}) \rightarrow \sigma^*(C - Br)$</td>
<td>(-0.44)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$n_y(\text{Br}) \rightarrow \text{Rydb.} A''(2)$</td>
<td>(0.42)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a^1A' \rightarrow f^1A'$</td>
<td>$n_z(\text{Cl}) \rightarrow \text{Rydb.} A'$</td>
<td>(-0.52)</td>
<td>8.72</td>
<td>97.0</td>
</tr>
<tr>
<td></td>
<td>$n_z(\text{Cl}) \rightarrow \sigma^*(C - Br)$</td>
<td>(-0.51)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$n_y(\text{Cl}) \rightarrow \sigma^*(C - Cl)$</td>
<td>(0.42)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a^1A' \rightarrow g^1A'$</td>
<td>$n_y(\text{Cl}) \rightarrow \text{Rydb.} A''(2)$</td>
<td>(0.66)</td>
<td>8.99</td>
<td>196.6</td>
</tr>
<tr>
<td></td>
<td>$n_y(\text{Cl}) \rightarrow \text{Rydb.} A''(1)$</td>
<td>(0.49)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$n_y(\text{Br}) \rightarrow \text{Rydb.} A''(1)$</td>
<td>(-0.45)</td>
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<td></td>
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<td>$a^1A' \rightarrow h^1A'$</td>
<td>$n_y(\text{Br}) \rightarrow \text{Rydb.} A''(2)$</td>
<td>(-0.75)</td>
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<td>148.0</td>
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<td>$n_y(\text{Cl}) \rightarrow \text{Rydb.} A''(1)$</td>
<td>(0.40)</td>
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<tr>
<td></td>
<td>$n_y(\text{Br}) \rightarrow \text{Rydb.} A''(1)$</td>
<td>(-0.45)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a^1A' \rightarrow i^1A'$</td>
<td>$n_z(\text{Cl}) \rightarrow \sigma^*(C - Cl)$</td>
<td>(-0.64)</td>
<td>9.57</td>
<td>76.0</td>
</tr>
<tr>
<td></td>
<td>$n_x(\text{Br}) \rightarrow \sigma^*(C - Br)$</td>
<td>(-0.43)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$n_x(\text{Br}) \rightarrow \sigma^*(C - Br)$</td>
<td>(-0.43)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a^1A' \rightarrow j^1A'$</td>
<td>$n_y(\text{Br}) \rightarrow \text{Rydb.} A''(1)$</td>
<td>(-0.68)</td>
<td>9.85</td>
<td>192.5</td>
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<td></td>
<td>$n_z(\text{Cl}) \rightarrow \text{Rydb.} A''(1)$</td>
<td>(-0.42)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$n_y(\text{Br}) \rightarrow \text{Rydb.} A''(2)$</td>
<td>(-0.40)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a^1A' \rightarrow k^1A'$</td>
<td>$n_x(\text{Br}) \rightarrow \sigma^* (C - Cl)$</td>
<td>(0.74)</td>
<td>10.62</td>
<td>81.6</td>
</tr>
</tbody>
</table>

aFor the ground state $<R^2>=72.7$

bFor the ground state $\omega=0.889$
Table 3.3: PMCAS and MS-CASPT2 calculated excitation energies (eV) with the corresponding main one-electron excitation, expectation values of $R^2$ (the specific expectation values of $x^2$, $y^2$ and $z^2$ for the Rydberg states are given in parenthesis), and oscillator strengths $f$, for the states of $A'$ symmetry of CH$_2$BrCl.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Principal Conf.</th>
<th>excitation energy (eV)</th>
<th>PMCAS</th>
<th>MS-CASPT2</th>
<th>$&lt;R^2&gt;$*</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a^1A' \rightarrow b^1A'$</td>
<td>$n_x(\text{Br}) \rightarrow \sigma^*(\text{C}-\text{Br})$</td>
<td>6.98</td>
<td>6.12</td>
<td>76.2</td>
<td>0.0071</td>
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<tr>
<td>$a^1A' \rightarrow c^1A'$</td>
<td>$n_z(\text{Cl}) \rightarrow \sigma^*(\text{C}-\text{Cl})$</td>
<td>7.66</td>
<td>7.18</td>
<td>74.9</td>
<td>0.0207</td>
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</tr>
<tr>
<td>$a^1A' \rightarrow d^1A'$</td>
<td>$n_x(\text{Br}) \rightarrow \text{Rydb.}A'$</td>
<td>8.29</td>
<td>7.42</td>
<td>118.5</td>
<td>0.0385</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(37.4, 44.1, 37.0)</td>
<td></td>
</tr>
<tr>
<td>$a^1A' \rightarrow e^1A'$</td>
<td>$n_z(\text{Cl}) \rightarrow \sigma^*(\text{C}-\text{Br})$</td>
<td>8.48</td>
<td>7.79</td>
<td>79.1</td>
<td>0.0023</td>
<td></td>
</tr>
<tr>
<td>$a^1A' \rightarrow f^1A'$</td>
<td>$n_z(\text{Cl}) \rightarrow \text{Rydb.}A'$</td>
<td>8.52</td>
<td>8.15</td>
<td>125.1</td>
<td>0.0233</td>
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<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>(38.7, 50.5, 35.9)</td>
<td></td>
</tr>
<tr>
<td>$a^1A' \rightarrow g^1A'$</td>
<td>$n_y(\text{Br}) \rightarrow \text{Rydb.}A''(1)$</td>
<td>9.03</td>
<td>8.19</td>
<td>142.4</td>
<td>0.0033</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>(40.3, 64.3, 37.8)</td>
<td></td>
</tr>
<tr>
<td>$a^1A' \rightarrow h^1A'$</td>
<td>$n_z(\text{Br}) \rightarrow \sigma^*(\text{C}-\text{Cl})$</td>
<td>9.11</td>
<td>8.59</td>
<td>77.7</td>
<td>0.1567</td>
<td></td>
</tr>
<tr>
<td>$a^1A' \rightarrow i^1A'$</td>
<td>$n_y(\text{Br}) \rightarrow \text{Rydb.}A''(2)$</td>
<td>9.33</td>
<td>9.09</td>
<td>173.8</td>
<td>0.0349</td>
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<tr>
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<td></td>
<td>(57.3, 76.2, 40.3)</td>
<td></td>
</tr>
<tr>
<td>$a^1A' \rightarrow j^1A'$</td>
<td>$n_y(\text{Cl}) \rightarrow \text{Rydb.}A''(1)$</td>
<td>9.88</td>
<td>9.16</td>
<td>173.6</td>
<td>0.0003</td>
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<td></td>
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<td></td>
<td>(57.3, 75.7, 40.6)</td>
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</tr>
<tr>
<td>$a^1A' \rightarrow k^1A'$</td>
<td>$n_y(\text{Cl}) \rightarrow \text{Rydb.}A''(2)$</td>
<td>10.47</td>
<td>9.88</td>
<td>197.6</td>
<td>0.0002</td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>(76.6, 79.4, 41.6)</td>
<td></td>
</tr>
</tbody>
</table>

*For the ground state $<X^2>=24.3$, $<Y^2>=24.8$, $<Z^2>=23.6$, $<R^2>=72.7$

The results for the $A'$ and $A''$ transitions at the highest level of theory employed (MS-CASPT2) are presented in Tables 3.3 and 3.4, respectively, together with the PMCAS energies. At this level of theory most of the valence-Rydberg mixing is cleared, as it can be noted in the values of the second moments, $R^2$, which for the valence states are always close to the ground state value. For the Rydberg states the specific expectation values of the $<x^2>$, $<y^2>$, $<z^2>$ are also given, in order to identify the polarization of the Rydberg transitions. The oscillator strengths of the respective states should also encompass the differences between valence and Rydberg states. Typically, Rydberg states possess transition dipole moments smaller than the valence states, since the overlap between atomic orbitals and valence orbitals is less effective than the overlap between two valence orbitals. In this case, however, some Rydberg states still show very intense bands.
Table 3.4: PMCAS and MS-CASPT2 calculated excitation energies (eV) with the corresponding main one-electron excitation, expectation values of $R^2$ (the specific expectation values of $x^2$, $y^2$ and $z^2$ for the Rydberg states are given in parenthesis), and oscillator strengths $f$, for the states of $A''$ symmetry of CH$_2$BrCl.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Principal Conf.</th>
<th>excitation energy (eV)</th>
<th>PMCAS</th>
<th>MS-CASPT2</th>
<th>$&lt;R^2&gt;^a$</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a^1A' \rightarrow a^1A''$</td>
<td>$n_y(\text{Br}) \rightarrow \sigma^*(C-\text{Br})$</td>
<td>7.02</td>
<td>6.04</td>
<td>81.7</td>
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<tr>
<td>$a^1A' \rightarrow b^1A''$</td>
<td>$n_y(\text{Cl}) \rightarrow \sigma^*(C-\text{Cl})$</td>
<td>7.60</td>
<td>7.11</td>
<td>78.5</td>
<td>0.0049</td>
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</tr>
<tr>
<td>$a^1A' \rightarrow c^1A''$</td>
<td>$n_y(\text{Br}) \rightarrow \text{Rydb.}A'$</td>
<td>8.26</td>
<td>7.40</td>
<td>125.7</td>
<td>0.0442</td>
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<td>(38.1, 49.46, 38.0)</td>
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<tr>
<td>$a^1A' \rightarrow d^1A''$</td>
<td>$n_y(\text{Cl}) \rightarrow \sigma^*(C-\text{Br})$</td>
<td>8.28</td>
<td>7.86</td>
<td>95.9</td>
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<tr>
<td>$a^1A' \rightarrow e^1A''$</td>
<td>$n_x(\text{Br}) \rightarrow \text{Rydb.}A''(1)$</td>
<td>8.46</td>
<td>8.17</td>
<td>146.2</td>
<td>0.0010</td>
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<tr>
<td>$a^1A' \rightarrow f^1A''$</td>
<td>$n_y(\text{Cl}) \rightarrow \text{Rydb.}A'$</td>
<td>9.05</td>
<td>8.22</td>
<td>129.9</td>
<td>0.0009</td>
<td></td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(37.4, 56.8, 35.7)</td>
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</tr>
<tr>
<td>$a^1A' \rightarrow g^1A''$</td>
<td>$n_y(\text{Br}) \rightarrow \sigma^*(C-\text{Cl})$</td>
<td>9.06</td>
<td>8.48</td>
<td>81.7</td>
<td>0.0024</td>
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</tr>
<tr>
<td>$a^1A' \rightarrow h^1A''$</td>
<td>$n_z(\text{Cl}) \rightarrow \text{Rydb.}A''(1)$</td>
<td>9.57</td>
<td>9.05</td>
<td>163.7</td>
<td>0.0006</td>
<td></td>
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<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>(46.5, 80.6, 36.6)</td>
<td></td>
</tr>
<tr>
<td>$a^1A' \rightarrow i^1A''$</td>
<td>$n_x(\text{Br}) \rightarrow \text{Rydb.}A''(2)$</td>
<td>9.88</td>
<td>9.16</td>
<td>193.2</td>
<td>0.0166</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(66.3, 84.9, 42.0)</td>
<td></td>
</tr>
<tr>
<td>$a^1A' \rightarrow j^1A''$</td>
<td>$n_z(\text{Cl}) \rightarrow \text{Rydb.}A''(2)$</td>
<td>9.97</td>
<td>9.83</td>
<td>203.3</td>
<td>0.0047</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(75.8, 86.5, 41.0)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$For the ground state $<X^2>=24.3$, $<Y^2>=24.8$, $<Z^2>=23.6$, $<R^2>=72.7$

Although at the MS-CASPT2 level all the states can be identified with an almost pure excitation, still some mixing of states is present. It is possible that even the present level of theory presents some artificial valence-Rydberg mixing or that the valence transitions for this molecule are very weak. Nevertheless, there is an evident correction on the ordering of the states predicted by the MS-CASPT2 energies and on the composition of the PMCAS wavefunction in comparison with the single root perturbed method. To best appreciate the effect of the dynamical correlation on the CASSCF wavefunction through single root or multistate CASPT2, the evolution of the main contribution of the wave function of each $A'$ state along with its corresponding vertical excitation energy at the three different levels of theory calculated in this work: CASSCF, SS-CASPT2 and MS-CASPT2, is illustrated in Fig. 3.3. As one can see, MS-CASPT2 includes most dynamical correlation,
CHAPTER 3. AB INITIO STUDY OF CH$_2$BRCL DISSOCIATION

Figure 3.3: Schematic representation of the change in energy of the excited states and corresponding wave function of the A’ states when going from CASSCF, to SS-CASPT2 and MS-CASPT2 level of theory. (Only the excitation with the main contribution on the wavefunction is shown for each root.)

as seen from the energy lowering with respect to the CASSCF values, which in some cases is enough to reverse the order of some states with respect to the order predicted by SS-CASPT2. These differences between single root and multistate CASPT2 may also reflect the artifacts of the approximation implicit in using SS-CASPT2 from SA-CASSCF orbitals. This is specially critical when the starting reference CASSCF wavefunction is not correct due to second order energy coupling terms between various electronic states, as it is the case when valence-Rydberg mixing is present at CASSCF level.

According to Tables 3.3 and 3.4, in both symmetries two valence excited states occur below the lowest Rydberg state. They correspond to the transitions $n_x$(Br)$\rightarrow \sigma^*(C-Br)$

### CASSCF

<table>
<thead>
<tr>
<th>DE / eV</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.92</td>
<td>$n_x$(Br)$\rightarrow \sigma^*(C-Br)$</td>
</tr>
</tbody>
</table>

### SS-CASPT2

<table>
<thead>
<tr>
<th>DE / eV</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.13</td>
<td>$n_y$(Br)$\rightarrow$ Rydb.$A''$(1)</td>
</tr>
<tr>
<td>9.12</td>
<td>$n_y$(Cl)$\rightarrow$ Rydb.$A''$(2)</td>
</tr>
<tr>
<td>8.72</td>
<td>$n_z$(Cl)$\rightarrow$ Rydb.$A'$</td>
</tr>
<tr>
<td>8.29</td>
<td>$n_z$(Cl)$\rightarrow \sigma^*(C-Br)$</td>
</tr>
<tr>
<td>8.13</td>
<td>$n_y$(Cl)$\rightarrow$ Rydb.$A''$(1)</td>
</tr>
<tr>
<td>7.57</td>
<td>$n_x$(Br)$\rightarrow$ Rydb.$A'$</td>
</tr>
</tbody>
</table>

### MS-CASPT2

<table>
<thead>
<tr>
<th>DE / eV</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.62</td>
<td>$n_x$(Br)$\rightarrow \sigma^*(C-Cl)$</td>
</tr>
<tr>
<td>9.85</td>
<td>$n_y$(Br)$\rightarrow$ Rydb.$A''$(1)</td>
</tr>
<tr>
<td>9.57</td>
<td>$n_z$(Cl)$\rightarrow \sigma^*(C-Cl)$</td>
</tr>
<tr>
<td>9.13</td>
<td>$n_y$(Br)$\rightarrow$ Rydb.$A''$(2)</td>
</tr>
<tr>
<td>8.99</td>
<td>$n_x$(Cl)$\rightarrow$ Rydb.$A''$(2)</td>
</tr>
<tr>
<td>8.72</td>
<td>$n_y$(Cl)$\rightarrow$ Rydb.$A'$</td>
</tr>
<tr>
<td>8.29</td>
<td>$n_z$(Cl)$\rightarrow \sigma^*(C-Br)$</td>
</tr>
<tr>
<td>8.13</td>
<td>$n_y$(Cl)$\rightarrow$ Rydb.$A''$(1)</td>
</tr>
<tr>
<td>7.57</td>
<td>$n_x$(Br)$\rightarrow$ Rydb.$A'$</td>
</tr>
<tr>
<td>7.35</td>
<td>$n_x$(Br)$\rightarrow$ Rydb.$A'$</td>
</tr>
<tr>
<td>6.20</td>
<td>$n_x$(Br)$\rightarrow \sigma^*(C-Br)$</td>
</tr>
<tr>
<td>6.12</td>
<td>$n_x$(Br)$\rightarrow \sigma^*(C-Br)$</td>
</tr>
</tbody>
</table>
calculated at 6.12 eV and \( n_z(\text{Cl}) \rightarrow \sigma^*(\text{C-Cl}) \) lying at 7.18 eV in \( \text{A}' \) symmetry and \( n_y(\text{Br}) \rightarrow \sigma^*(\text{C-Br}) \) at 6.04 eV and \( n_y(\text{Cl}) \rightarrow \sigma^*(\text{C-Cl}) \) at 7.11 eV in \( \text{A}'' \) symmetry. According to Orkin et al. [27] the experimental UV spectrum of \( \text{CH}_2\text{BrCl} \) has a maximum cross-section at 202.6 ± 0.5 nm (6.1 eV) which according to the MS-CASPT2 results can be assigned to \( n(\text{Br}) \rightarrow \sigma^*(\text{C-Br}) \) transitions. These states were placed by SS-CASPT2 higher by ca. 0.1 eV. From the measured UV spectrum the oscillator strength belonging to this peak was estimated in appendix 5.2 by fitting a Gaussian function for the spectrum transformed from wavelength to energy domain. The resulted experimental value for \( f \) is about 0.0126. Since the excitation energies to the \( b_1^A \text{A}' \) and \( a_1^A \text{A}'' \) states lie very close to each other, the measurement cannot resolve these two transitions, thus the value of \( f \) should correspond roughly to the sum of the theoretical oscillator strengths 0.0071 (for \( b_1^A \text{A}' \)) and 0.0078 (for \( a_1^A \text{A}'' \)), i.e. to 0.0149. Although the effect of the temperature (298 K) at which the spectrum was measured is ignored here, the computed oscillator strength agrees well with the one deduced from the measured spectrum. Unfortunately no absorption cross sections were measured below 187 nm, but the experimental absorption profile shows an absorption increase starting at 192 nm, which according to our results must correspond to the onset of the \( n_z(\text{Cl}) \rightarrow \sigma^*(\text{C-Cl}) \) absorption band. According to this assignment, the \( n(\text{Cl}) \rightarrow \sigma^*(\text{C-Cl}) \) band appears at higher wavelengths (173 nm) than it can be estimated from \( \text{CF}_2\text{BrCl} \) (164 nm) [83]. At 7.4 eV lies the lowest Rydberg state \( n(\text{Br}) \rightarrow \text{Ryd} \text{b A}', \) almost degenerated in both symmetries, with a predicted oscillator strength of 0.04. The nature of the transitions in the \( \text{A}' \) and \( \text{A}'' \) spectrum are very similar in the light of the two near-degenerate lone pair molecular orbitals, and since the \( \text{A}' \) counterparts show more intense peaks than the \( \text{A}'' \) ones, from now on we will focus mostly on the \( \text{A}' \) transitions. Another shoulder should be present in the spectrum at 7.8 eV due to the \( e^1\text{A}' \) state designated as \( n_x(\text{Br}) \rightarrow \sigma^*(\text{C-Cl}) \) transition. In the present assignment the PMCAS oscillator strength is very weak, cf. Table 3.3. One reason for that could be that this state comes from the SS-CASPT2 \( e^1\text{A}' \) state computed with a reference weight of 0.85, low in comparison with the ground state value 0.89. The next electronic transitions are two Rydberg states from the Cl and Br lone pairs, in increasing order of energy, respectively. They conform the \( f^1\text{A}' \) and \( g^1\text{A}' \) or \( e^1\text{A}'' \) and \( f^1\text{A}'' \) states, predicted almost degenerated at ca. 8.2 eV, in both \( \text{A}' \) and \( \text{A}'' \) symmetries. These states are placed by MS-CASPT2 ca. 0.3 eV higher in energy with respect to the single root CASPT2, to compensate the decrease of energy in the valence states lying below (cf. Fig. 3.3). The next valence state, \( h^1\text{A}' \), corresponding to the \( n_x(\text{Br}) \rightarrow \sigma^*(\text{C-Cl}) \) transition, is predicted very intense at both MS-CASPT2 (see Table 3.3) and CASSCF level (see \( k^1\text{A}' \) in Table 3.2),
with an oscillator strength of ca. 0.15. This state is calculated at 8.6 eV, at both single and multistate CASPT2 level. At higher energies, above 9 eV, lie three different Rydberg states with decreasing oscillator strengths, suggesting that these states should have little or no contribution to the absorption spectrum.

All the calculated valence transitions in CH$_2$BrCl involve promotions from the lone pairs of the Cl or Br atoms to the antibonding $\sigma^*$ orbitals on the carbon-halogen (C-X) bond. Such excitations are generally repulsive, mostly leading to direct carbon-halogen bond cleavage. The lowest states, corresponding to $n$(Br)$\rightarrow$ $\sigma^*$(C-Br) and $n$(Cl)$\rightarrow$ $\sigma^*$(C-Cl) transitions along the C-Br and C-Cl coordinates, respectively, are therefore expected to be strongly repulsive and should cross at a certain point, which implies that absorption into these states should lead to a fast photodissociation producing corresponding CH$_2$Cl and CH$_2$Br fragments. MS-CASPT2 potential scans along the C-Cl and C-Br coordinates were performed in order to confirm the nature of the potential energy curves and to use them for investigation of the laser-driven photodissociation dynamics by numerical wavepacket simulations. The results of these computations will be reported in the following sections.

### 3.4 Electron configurations in the dissociation limit

In the present section computations for the dissociated states are discussed and compared to the literature. For these calculations as well as for those of the potential curves discussed in the next section, the same method (MS-CASPT2) was used with the same active space as in the previous section. The only difference is, that only 9 roots were involved into the computations at the dissociation limit and also for the potential scan for internuclear distances larger than 2.65 Å, for all the lowest 9 roots where already valence excitations. Potential energy curves were computed in relatively small steps up to the internuclear distance of 10 Å (see the next section). Apart from the diabatic curve correlated with the ionic dissociation channel (CH$_2$XY $\rightarrow$ CH$_2$X$^+$ + Y$^-$), the potential energies of the states involved into the computations do not change any more for larger CH$_2$X−Y distances. The electronic states of the dissociated molecule were determined at C−Y=50 Å for both Y=Cl and Br, for two different geometries: once for the non-relaxed geometry, inherited from the original equilibrium geometry of the CBM and once for the relaxed geometries of the CH$_2$X radicals. Computations for the relaxed geometries were initiated from the results of the non-relaxed ones. For the relaxed geometry the ground state equilibrium geometries of the radicals optimized by Li and Francisco at the CCSD(T)/6−311 + +G(3df,3pd) level of theory were used. [109] Unlike the non-relaxed geometries, both
radicals have a planar structure in their ground electronic states in equilibrium. The optimized geometry-parameters reported in Ref. [109] are $r(C-H) = 1.076 \, \tilde{A}$, $r(C-Cl) = 1.696 \, \tilde{A}$ and $\theta(HCCl) = 117.8^\circ$ for the CH$_2$Cl and $r(C-H) = 1.075 \, \tilde{A}$, $r(C-Br) = 1.851 \, \tilde{A}$ and $\theta(HCBr) = 117.9^\circ$ for the CH$_2$Br. In the following only the MS-CASPT2 results will be presented, since they were found to be almost exactly the same as the SS-CASPT2 ones. As in the calculations discussed in the previous section, the level shift (LS) method was used to avoid intruder states. The same LS value (0.3 au) as applied for the equilibrium geometry computations was used for the C–Cl=50 Å computations. In case of the C–Br=50 Å computations, a higher LS value (0.4 au) had to be used in order to get a balanced description. The reference weights were then between 0.91 and 0.88 for each SS-CASPT2 root.

From the MS-CASPT2 results for the equilibrium and the dissociated geometries of the CBM molecule, the dissociation energies in the ground electronic state can be computed. In this case the energies of the dissociated states were compared to ground state energy of the parent molecule in equilibrium obtained by using 9 roots in the computation for the sake of consistency. For the non-relaxed geometries the dissociation energies are 3.22 eV for the C–Br channel and 3.71 eV for the C–Cl channel. The dissociation energies computed between the relaxed geometries are 2.99 eV and 3.47 eV for the C–Br and C–Cl channels, respectively. These are very close to the experimental values for the dissociation energies of CH$_2$Cl–Br and CH$_2$Br–Cl which are 285 kJmol$^{-1}$ (2.95 eV) and 331 kJmol$^{-1}$ (3.43 eV), respectively. [28, 32] The differences between dissociation energies belonging to the non-relaxed ground state potentials and the values obtained for the relaxed geometries of the radicals are about 0.23 eV in both channels. These differences do not influence the dissociation dynamics as long as dissociation into the electronic ground state of the radicals is considered, i.e., as long as the parent molecule is dissociated in the first excited electronic state. Excitation energies and electronic configurations, however, strongly depend on the geometry of the CH$_2$X radical.

The different electronic states and corresponding energies of the CH$_2$Cl + Br system at C–Br=50 Å are given in Table 3.5. The left and the right hand side of the table contains the results using the non-relaxed- and relaxed ground state CH$_2$Cl geometries, respectively. The fact, that we performed the computation for the total CH$_2$X + Y system
Table 3.5: MS-CASPT2 calculated transition energies in eV with their corresponding one-electron excitations, for the states of \( \text{A}' \) symmetry of \( \text{CH}_2\text{BrCl} \) at the dissociation limit \( \text{C-Br}=50 \text{ Å} \). On the left hand side the results obtained for the non-relaxed geometry are presented while in the right hand side the results with the relaxed geometry of the \( \text{CH}_2\text{Cl} \) radical are given (see text).

<table>
<thead>
<tr>
<th>Tr.</th>
<th>Principal Conf.</th>
<th>( \Delta E )</th>
<th>Tr.</th>
<th>Principal Conf.</th>
<th>( \Delta E )</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a^2A^+ )</td>
<td>( n_y(\text{Cl}) \rightarrow \pi_z^*(\text{C-Cl}) )</td>
<td>4.39</td>
<td>( b^2A' )</td>
<td>( \pi_z^<em>(\text{C-Cl}) \rightarrow \sigma^</em>(\text{C-Cl}) )</td>
<td>5.14 (5.23) (^a)</td>
<td>0.0004</td>
</tr>
<tr>
<td>( b^2A' )</td>
<td>( \pi_z(\text{C-Cl}) \rightarrow \pi_z^*(\text{C-Cl}) )</td>
<td>5.24</td>
<td>( a^2A^+ )</td>
<td>( n_y(\text{Cl}) \rightarrow \pi_z^*(\text{C-Cl}) )</td>
<td>5.19 (5.35)</td>
<td>0.0000</td>
</tr>
<tr>
<td>( c^2A' )</td>
<td>( \pi_z^<em>(\text{C-Cl}) \rightarrow \sigma^</em>(\text{C-Cl}) )</td>
<td>5.61</td>
<td>( \text{CH}_2\text{Cl}^++\text{Br}^- )</td>
<td>5.38</td>
<td>0.0000</td>
<td></td>
</tr>
<tr>
<td>( b^2A^* )</td>
<td>( \pi_z^<em>(\text{C-Cl}) \rightarrow \sigma^</em>(\text{C-H}) )</td>
<td>6.16</td>
<td>( \text{CH}_2\text{Cl}^++\text{Br}^- )</td>
<td>6.30 (6.51)</td>
<td>0.0459</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Results in parentheses are calculated by Li and Francisco at MRCI level of theory [109].

Instead of computing the \( \text{CH}_2\text{X} \) radical only, resulted sometimes in degenerated states for the neutral dissociation channels. In fact, apart from the ion-pair state, which is constituted by \( \text{CH}_2\text{X}^+ \) and \( \text{Y}^- \) ions, each state is three times degenerated for the \( \text{CH}_2\text{X}+\text{Y} \) system, since the partially occupied \( p \) orbital of the cleaved atom, \( \text{Y} \), may have three linearly independent spatial orientations. These different orientations represent only rotations of the coordinates of the cleaved atom which do not influence the electronic configuration of the \( \text{CH}_2\text{X} \) radical. As a result, computing only the \( \text{A}' \) symmetry states of the total system \( \text{CH}_2\text{X}+\text{Y} \), both the \( \text{A}' \) and \( \text{A}'' \) symmetry states of the \( \text{CH}_2\text{X} \) radical were obtained. The ion-pair state, nevertheless, unique and have \( \text{A}' \) symmetry. Due to the degeneracies, only the first four excited states of the radicals are obtained with 9 roots. The ion-pair state, \( \text{Br}^-+\text{CH}_2\text{Cl}^+ \), appears as the third and the fourth excitation for relaxed and non-relaxed geometries of the radical, respectively. The corresponding energy for the relaxed case, should then be equal to the difference between the vertical ionisation potential of the \( \text{CH}_2\text{Cl} \) radical (8.88 eV [110]) and the electron affinity of the \( \text{Br} \) atom (3.364 eV [54]). This difference is 5.516 eV in acceptable agreement with our results of 5.38 eV. The rest of the roots describe different excitations of the neutral radical. In parentheses the excitation energies computed by Li and Francisco for the relaxed geometry are presented for comparison. They performed CASSF and MRCI computations using a CAS active space of 13 electrons correlated in 10 orbitals. The values given in parentheses correspond to their MRCI results.

For the sake of clarity, the electronic excitations are schematically depicted with atomic
orbitals in Fig. 3.4 for the radicals in their relaxed geometries together with the lowest excitations of the parent molecule. The electronic configurations of the first two excited states of the CH$_2$Cl radical with relaxed geometry are the same as those obtained by Li and Francisco. [109] In both set of calculations, the $\pi^*_z$(C−Cl) has a major contribution from the 2p$_z$(C) and the $\pi_z$(C−Cl) is dominated by the 3p$_z$(Cl). The MS-CASPT2 excitation energies for the first two roots are somewhat lower than those reported in Ref. [109] at the MRCI level. In general the transition energies obtained through the MRCI approach are overestimated with respect to the MS-CASPT2 transition energies. These trends have been previously observed and discussed for some transition metal complexes [111]. The transition $\pi^*_z$(C−Cl) → $\sigma^*$(C−H), which is at MS-CASPT2 the third singlet excited state of the neutral radical is missing by Li and Francisco. The first transition has a very low oscillator strength and the second transition is forbidden. Similarly, the oscillator strength of the $\pi^*_z$(C−Cl) → $\pi^*_z$(C−Cl) transition is also zero. Thus the first peak in the experimental UV spectrum is expected to belong to the fourth excitation, which has a character of $\pi_z$(C−Cl) → $\pi^*_z$(C−Cl) and has an oscillator strength of 0.0459, which is two orders of magnitude larger than the first nonzero oscillator strengths. This $\pi_z$(C−Cl) → $\pi^*_z$(C−Cl) transition appears as the third one in Ref. [109] with an excitation energy of 6.51 eV. The corresponding transition energy at MS-CASPT2 is again lower: 6.30 eV. Indeed, the first absorption peak of the UV-spectrum of CH$_2$Cl radical was measured by Roussel et.al. [112] at 200 nm (6.20 eV) in a better agreement with the MS-CASPT2 6.30 eV transition energy than with the 6.51 eV value of Ref. [109]. As in the case of the parent molecule, we have also estimated the oscillator strength from the spectrum of the CH$_2$Cl radical, measured by Roussel et. al. [112] at around 200 nm. (see appendix 5.2) Since the measured data did not allow an accurate fit, especially not in the low wavelength region, the deduced oscillator strength of 0.0852 is probably far overestimated. Nevertheless it is still much closer to the MS-CASPT2 estimated value of 0.0459 than to the value of 1.47 from Ref. [109].

The MS-CASPT2 results for the CH$_2$Br radical at C−Cl=50 Å are given in Table 3.6. The corresponding MRCI energies computed in Ref. [109] are given in parentheses. In this case, the degeneracies allowed the computation of only four different electronic states, including the ion-pair state, within the considered 9 roots. The electronic configurations of the first three excited states are analogous to those obtained previously for the C−Br=50 Å case. In the present case, however, the ionic dissociation channel, CH$_2$Br$^+ +$ Cl$^-$, do not appear within the first four excited states for the non-relaxed CH$_2$Br geometry, but it ap-
Figure 3.4: Electronic configurations of CH$_2$BrCl, CH$_2$Br, and CH$_2$Cl. Only the lone pairs of the halogen atoms (X=Br, Cl) and the $\sigma, \sigma^*$ and $\pi, \pi^*$ C-X orbitals are sketched in their corresponding orientations. The C-H orbitals are skipped for the sake of clarity; therefore, the $b^2A^\prime$ state of CH$_2$Cl is not shown.

appears as the third root again for the relaxed geometry. If we subtract the electron affinity of the Cl atom (3.613 eV [54]) from the vertical ionisation potential of the CH$_2$Br
Table 3.6: MS-CASPT2 calculated transition energies in eV with their corresponding one-electron excitations, for the states of A’ symmetry of CH$_2$BrCl at the dissociation limit, i.e., at C-Cl=50 Å. On the left hand side the results obtained for the non-relaxed geometry are presented while in the right hand side the results with the relaxed geometry of CH$_2$Br radical are given (see text).

<table>
<thead>
<tr>
<th>Non-relaxed CH$_2$Br geometry</th>
<th>Relaxed CH$_2$Br geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tr.</td>
<td>Principal Conf.</td>
</tr>
<tr>
<td>a$^2$A$^\pi$</td>
<td>$n_y$(Br) → $\pi_x$(C-Br)</td>
</tr>
<tr>
<td>b$^2$A$'$</td>
<td>$\pi_x$(C-Br) → $\pi_x^*$ (C-Br)</td>
</tr>
<tr>
<td>c$^2$A$'$</td>
<td>$\pi_x^<em>$ (C-Br) → $\sigma^</em>(C-Br)$</td>
</tr>
<tr>
<td>d$^2$A$'$</td>
<td>$\sigma$(C-Br) → $\pi_x^*$ (C-Br)</td>
</tr>
</tbody>
</table>

$^a$Results in parentheses are calculated by Li and Francisco at MRCI level of theory [109].

radical (8.75 eV [110]) we get 5.14 eV. This is again in acceptable agreement with the MS-CASPT2 energy of 4.98 eV obtained for this electronic configuration. Similar to the CH$_2$Cl–Br case, the rest of the states describe different valence transitions in the CH$_2$Br radical (see Fig. 3.4).

The first three excited electronic states of the neutral radical for the relaxed geometry were found to be the same as those reported in Ref. [109] again predicted at lower energies. The $\pi_x$(C-Br) has a major contribution from the Br, while in $\pi_x^*$ (C-Br) the major contribution is from the C, similar to Ref. [109]. Again the first transition for the relaxed CH$_2$Br radical has a low oscillator strength and the next transition is forbidden. Therefore, the first peak in the UV-spectrum of CH$_2$Br can be assigned to the third excitation, i.e., to $\pi_x$(C-Br) → $\pi_x^*$ (C-Br), which has an oscillator strength of 0.0452, again about two orders of magnitude larger than the oscillator strength of the first transition. The UV spectrum of CH$_2$Br was measured by Villenave and Lesclaux [113]. They found the first absorption peak at around 230 nm at 298 K. This corresponds to an excitation energy of 5.39 eV in much better agreement with our MS-CASPT2 energy of 5.38 eV than with the value of 5.62 eV computed in Ref. [109] for this transition. In appendix 5.2 the oscillator strength for the first peak in the UV spectrum of CH$_2$Br radical measured by Villenave and Lesclaux [113] was also estimated. The measured data could be nicely fitted and a value of $f=0.0491$ was obtained, in excellent agreement with the MS-CASPT2 $f=0.045$. It should be noted, however, that the effect of the temperature (295 K) at which the spectrum was measured has been ignored.
3.5 Potential energy- and transition dipole moment curves

In the present section the computed one dimensional non-relaxed potential energy curves along the C−Br and C−Cl reaction coordinates are discussed. In either case only one parameter was changed, the C−Br or the C−Cl bond length, respectively, whereas the rest of the parameters were frozen to the equilibrium values given in section 3.3. As shown in section 3.3, the nature of the transitions of A’ and A” symmetry is very similar due to the near degeneracy of the lone pairs molecular orbitals. The strength of the A’ excitations is either similar or considerably stronger than that of their A” counterparts, henceforth we focus exclusively on the A’ states. Furthermore, due to the short time scale in which dissociation takes place, intersystem crossing is not competitive and therefore, triplet states are not considered.

The potential energy curves of A’ symmetry for the electronically singlet states were computed at the MS-CASPT2 level of theory, using the same active space (i.e., 12 electrons in 12 orbitals), as employed in the vertical excitation energies of the CH$_2$BrCl, CH$_2$Br and CH$_2$Cl species. As discussed in section 3.3, 11 roots are needed to correctly describe the low-energy valence states at the Franck-Condon region due to the low lying Rydberg states. At larger internuclear separations, however, Rydberg states disappear, and only valence excitations occur within the first nine roots. Therefore, in both directions 11 roots were used for C−X<2.65 Å internuclear separations but 9 roots for C−X>2.65 Å. Apart from a small constant shift in all the energies, which has been eliminated, the 11 root curves and the 9 root ones nicely match. In order to avoid the occurrence of intruder states, the level shift technique was applied. All along the C−Cl bond the same level shift (LS=0.3 au) used for the equilibrium CBM geometry ensured reliable CASSCF reference weights during the CASPT2 calculations and resulted in converged correlated energies. For the C−Br direction, we used LS=0.4 au for C−Br>3 Å as we did in the case of the dissociated state, C−Br=50 Å. Only with this higher LS value we could get reliable CASSCF reference weights and the real energy of the diabatic state belonging to the transition $n_y$(Cl)+$n_y$(Br) → $\sigma^*$(C−Br), which appears as the ninth root at around C−Br=2.5 Å and correlates to the first excited state, $n_y$(Cl) → $\pi^*_z$(C−Cl) of the CH$_2$Cl radical for its non-relaxed geometry.

Figs. 3.5a) and b) show the lowest four adiabatic potential energy curves for the C−Cl and C−Br directions, respectively. To get a better insight into the details of the curves at small internuclear distances, a logarithmic horizontal axis was chosen. Cubic splines were
Figure 3.5: Figures a) and b) show 1 dimensional adiabatic potential curves for the four lowest electronic states of A’ symmetry in the C-Cl and C-Br directions, respectively. The symbols represent the energy values computed at the MS-CASPT2 level of theory with cubic spline fit for the lowest three states.

fitted to the ground- and to the first two electronic excited states. The first points computed along the C−Cl and C−Br bonds were at 1.6 Å and 1.65 Å, respectively. The fitted curves were extrapolated towards even smaller internuclear distances somewhat arbitrarily. This extrapolation, however, does not influence the dynamics of the photodissociation. As expected from the analysis of the vertical spectrum at the ground-state equilibrium geometry of the CBM, the first (adiabatic) excited state (b\(^1\)A’) is directly dissociative in the C−Br direction (see Fig. 3.5b). On the other hand, this state seems to be dissociative in the C−Cl direction, too. An avoided crossing between b\(^1\)A’ and c\(^1\)A’ states is present at ca. 1.9 Å, and as a consequence the b\(^1\)A’ state is less steep in the C−Cl direction than in the C−Br one, indicating preferential C−Br bond fission after excitation to the first electronic excited state. This is in agreement with the experimental observations. [28, 32] The second excited state of the molecule (c\(^1\)A’) is bounded in both directions assuming resonant excitations. Nevertheless, two aspects should be considered in the wavepacket-dynamics on this excited state: i) the non-adiabatic coupling with other potentials, and ii) the fact that the present potentials are one dimensional and non-relaxed. It is known that the first electronic excited state of both CH\(_2\)Cl and CH\(_2\)Br radicals is strongly dissociative for the halogen atom. [109] This suggests, that the third adiabatic potential, c\(^1\)A’ is open for the CH\(_2\)ClBr → CH\(_2\) + Br + Cl dissociation. We have computed the ground state energy of the non-relaxed CBM imposing a C−Br=C−Cl=10 Å distance, finding a MS-CASPT2 energy of 7.18 eV with respect to the ground state energy of the CBM.
at equilibrium geometry, i.e., the same as the vertical excitation energy of the $c^1A'$ state for the CBM (see Table 3.3). Considering geometry-relaxation, this computation confirms the possibility of the $\text{CH}_2\text{ClBr} \rightarrow \text{CH}_2 + \text{Br} + \text{Cl}$ dissociation in the state $c^1A'$. However, this possibility can only be confirmed by measurements or by the complete computation of the two dimensional $c^1A'$ surface.

More important for us are the possible effects of non-adiabatic couplings on the wavepacket dynamics after an excitation to the $c^1A'$ state. Since the energy of the $d^1A'$ adiabatic state lies above the resonant excitation energy (7.18 eV) of the $c^1A'$ state along the whole $C$–$\text{Cl}$ and $C$–$\text{Br}$ coordinates (see Fig. 3.5), it may be assumed that population transfer to this adiabatic state do not occur through potential coupling. Therefore, the $d^1A'$ state will be excluded from the investigation of the one-photon photodissociation of the CBM. The effect of the crossing between the excited states $c^1A'$ and $b^1A'$, corresponding to the $n_z(\text{Cl}) \rightarrow \sigma^*(C-\text{Cl})$ and $n_x(\text{Br}) \rightarrow \sigma^*(C-\text{Br})$ excitations, respectively, in the FC region, will be investigated in section 3.6. This crossing takes place at around $C$–$\text{Cl}=1.91$ Å on the one dimensional potential curve, i.e., very close to the Franck-Condon window. The corresponding minimum separation of the adiabatic $b^1A'$ and $c^1A'$ potential curves is 0.37 eV. In order to describe the population transfer through this crossing, the potentials have been diabatized. Although other crossings are present in the system, (cf. Fig. 3.6 and 3.7) only the $b^1A'/c^1A'$ crossing have been considered because this appears to be the crucial crossing which might be responsible for controlling $C$–$\text{Cl}$ bond dissociation. [39]

Moreover, a complete diabatization including all the states require very demanding quantum chemical computations with a very fine resolution. Nevertheless, the analysis of the vertical excitations at the equilibrium and at the dissociation limit (see sections 3.3 and 3.4) as well as a careful analysis of the wavefunction at intermediate nuclear separations, allow to deduce a schematic picture of the diabatics contributing to the $b^1A'$ and $c^1A'$ adiabatic curves. This schematic picture is shown in Fig. 3.6 and 3.7 for the $C$–$\text{Cl}$ and $C$–$\text{Br}$ potential scans, respectively. It should be noticed, that only those diabatics, that contributed to the first two adiabatic excited states at the Franck-Condon region or after it are shown in these figures.

Let us investigate the potential curves in the $C$–$\text{Cl}$ direction first. As shown in Fig. 3.6, two diabatics contribute to the first adiabatic excited state, $b^1A'$: the $n_x(\text{Br}) \rightarrow \sigma^*(C-\text{Br})$ and $n_z(\text{Cl}) \rightarrow \sigma^*(C-\text{Cl})$ denoted by $b$ and $c$ in the figure. This crossing is the most important from the point of view of the wavepacket-dynamics in the adiabatic excited state $c^1A'$. The adiabatic curve $c^1A'$ is formed by several diabatics. In the FC-region it is determined by the diabatic $c$, which correlates with the ground state of the dissociation products, $\text{CH}_2\text{Br} +$
Main configurations of the diabatic potentials:

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>$n_x(Br) \rightarrow \text{Ryd} A'$</td>
</tr>
<tr>
<td>b</td>
<td>$n_x(Br) \rightarrow \sigma^*(C-Br)$</td>
</tr>
<tr>
<td>c</td>
<td>$n_z(Cl) \rightarrow \sigma^*(C-Cl)$</td>
</tr>
<tr>
<td>d</td>
<td>$n_x(Br) \rightarrow \sigma^*(C-Cl)$</td>
</tr>
<tr>
<td>e</td>
<td>$\sigma(C-Cl) \rightarrow \sigma^*(C-Cl)$</td>
</tr>
<tr>
<td>f</td>
<td>$n_y(Cl)+n_y(Br) \rightarrow \sigma^*(C-Cl)$</td>
</tr>
</tbody>
</table>

Figure 3.6: Schematic picture of those (and only those!) diabatic states that contribute to the lowest two excited adiabatic potential energy curves. The adiabatic curves are displayed with solid lines, while the diabatics are displayed with dashed lines.

Cl. Before the FC-region there is a contribution from the lowest Rydberg state, $n_x(Br) \rightarrow \text{Ryd} A'$, denoted by a in the figure. Right after the FC-transition another crossing occurs between the diabatic b and d, the later assigned to the configuration, $n_x(Br) \rightarrow \sigma^*(C-Cl)$, which is the 7th excited state of symmetry $A'$ at equilibrium geometry. This diabatic state correlates with the second excited state, $\pi_x(C-Br) \rightarrow \pi_x^*(C-Br)$, of the CH$_2$Br fragment in the non-relaxed dissociation limit (see Table 3.6). The last two contributions come from the diabatic states e and f, the former assigned to the configuration $\sigma(C-Cl) \rightarrow \sigma^*(C-Cl)$ which correlates with the ionic dissociation channel, CH$_2$Br$^+ + Cl^-$. The latter, f, corresponds to a double excitation in the parent molecule from the two lone pair orbitals of $A''$ symmetry on the halogen atoms, i.e., $n_y(Cl)+n_y(Br) \rightarrow \sigma^*(C-Cl)$. This correlates in the non-relaxed dissociation limit with the first excited state of the CH$_2$Br radical, i.e., with $n_y(Br) \rightarrow \pi_x^*(C-Br)$. The extremely small energy gap between the curves e and f in the vicinity of the crossing between ca. 5.6 and 5.8 Å, indicates that this crossing is rather non-avoided, resulting in a very low probability of population transfer from one diabatic curve to the other.

The diabatic contributions to the adiabatic potentials in the other direction, i.e., along the C–Br bond show strong similarities with the diabatic structure discussed before. The a, b and c denote the same electron configurations in Fig. 3.6 as in Fig. 3.7, i.e., $n_x(Br) \rightarrow \text{Ryd} A', n_x(Br) \rightarrow \sigma^*(C-Br)$ and $n_z(Cl) \rightarrow \sigma^*(C-Cl)$, respectively. The adiabatic states d, e and f in the C–Br direction are analogous to the corresponding states in the C–Br direction. This means that they refer to the following electron configurations.
Main configurations of the diabatic potentials:

- **a**: $n_x(\text{Br}) \rightarrow \text{Rydb. } A'$
- **b**: $n_x(\text{Br}) \rightarrow \sigma^*(\text{C–Br})$
- **c**: $n_z(\text{Cl}) \rightarrow \sigma^*(\text{C–Br})$
- **d**: $n_z(\text{Cl}) \rightarrow \sigma^*(\text{C–Cl})$
- **e**: $\sigma(\text{C–Br}) \rightarrow \sigma^*(\text{C–Br})$
- **f**: $n_y(\text{Cl})+n_y(\text{Br}) \rightarrow \sigma^*(\text{C–Br})$

Figure 3.7: Schematic picture of the diabatic states contributing to the lowest two excited adiabatic potential energy curves. The adiabatic curves are displayed with solid lines, while the diabatics are displayed with dashed lines.

In Fig. 3.7: State $d$ has a nature of $n_z(\text{Cl}) \rightarrow \sigma^*(\text{C–Br})$ correlating with the second excited state of the non-relaxed CH$_2$Cl fragment in the dissociation limit. State $e$ denotes the configuration $\sigma(\text{C–Br}) \rightarrow \sigma^*(\text{C–Br})$ correlating with the ionic dissociation channel, CH$_2$Cl$^+$ + Br$^-$, while state $f$ is $n_y(\text{Cl})+n_y(\text{Br}) \rightarrow \sigma^*(\text{C–Br})$ correlating with the first excited state of the non-relaxed CH$_2$Cl fragment, $n_y(\text{Cl}) \rightarrow \pi^*_z(\text{C–Cl})$. Again the crossing between $e$ and $f$ at C–Br = 6 Å seems to be not-avoided. The energy difference at this point was found to be less than 0.013 eV.

In order to simulate the photodissociation process, the transition dipole moment (TDM) values should also be known as a function of the internuclear distance. These quantities were computed in the same way as described in section 3.3 for the equilibrium geometry. The nonzero components ($x$ and $z$) of the transition dipole moment vectors between the first two adiabatic excited states of symmetry $A'$ and the electronic ground state $a_1A'$ are presented in Figs. 3.8 and 3.9. For each reaction coordinate, the FC-transition is indicated by a vertical line. The computed values are displayed by the symbols while the connecting line represents a cubic spline fit to these points. In case of the C–Cl bond stretching the TDM values for the $b^1A' \rightarrow c^1A'$ transition are also displayed in Fig. 3.9c), since this transition may play an important role when the coherent control of the dissociation is considered, as will be done in section 3.7. As already indicated by the oscillator strengths obtained for the equilibrium geometry in section 3.3, the $a^1A' \rightarrow c^1A'$ transition is considerably stronger than the transition into the first excited state ($a^1A' \rightarrow b^1A'$). According to Figs. 3.8 and 3.9 the same is true for intermediate internuclear...
Figure 3.8: Transition dipole moments for transitions between adiabatic states as a function of C-Br distance. Figures a) and b) display the components of the TDM for transitions $a^1A' \rightarrow b^1A'$ and $a^1A' \rightarrow c^1A'$, respectively. Solid and dashed lines belong to x and z components of the TDM, respectively.

Figure 3.9: Transition dipole moments for transitions between adiabatic states as a function of C-Cl distance. Figures a) – c) display the components of the TDM for transitions $a^1A' \rightarrow b^1A'$, $a^1A' \rightarrow c^1A'$ and $b^1A' \rightarrow c^1A'$, respectively. Solid and dashed lines belong to x and z components of the TDM, respectively.
distances. In both directions the TDM of the $a^1A' \rightarrow b^1A'$ transition takes its maximum value in the vicinity of the FC-region. This transition dipole moment is parallel to the Z axis, i.e., to the C–Br bond in the FC-region which indicates that the transition to the first excited state is a parallel transition. The peaks of the transition dipole moment curves are the results of the aforementioned crossings. The peak of the z-component of the TDM for the $a^1A' \rightarrow b^1A'$ transition along the C–Br distance (cf. Fig. 3.8a)) indicates the crossing between diabatics $a$ and $b$ shown in Fig. 3.7. In the C–Cl direction, the peak of both TDM components for this transition at around C–Cl=1.9 Å indicates the crossing between the diabatics $b$ and $c$.\(^7\) The smaller local maximum of both components of the $a^1A' \rightarrow c^1A'$ transition along the C–Cl direction at the equilibrium geometry reflects the crossing between diabatics $a$ and $c$ displayed in Fig. 3.6. The overall maximum of both components of $a^1A' \rightarrow c^1A'$ at C–Cl = 3 Å is due to the crossing between diabatics $e$ and $d$ at around C–Cl = 2.8 Å (see Fig. 3.6). Similarly, in the C–Br direction the maximum of the TDM belonging to $a^1A' \rightarrow c^1A'$ is again due to the crossing between diabatics $e$ and $d$ (see Fig. 3.7). Hence, as a conclusion we may say, that the shape of the TDM curves confirms the schematic picture of the diabatics proposed by analyzing the electron configurations and displayed in Figs. 3.6 and 3.7.

3.6 Quantum dynamical results and discussion

With the help of the ab initio potential energy curves, $V_{a_{ii}}(Q)$, obtained in the previous section (cf. Fig. 3.5), the spatio-temporal evolution of the wavefunctions (and thus the populations) in the different electronic states were simulated by solving the one-dimensional TDSE numerically separately for the C–Br and C–Cl directions. The components of the transition dipole moment vectors, $\mu_{a_{ij}}(Q)$ used in the simulations have been also determined (cf. Figs. 3.8 and 3.9). Although these simulations are based on the accurate ab initio data, they should be regarded as preliminary for two reasons. i) The dynamics is essentially multidimensional and thus the physical relevance of the 1D approximation is limited.\(^8\) ii) The A" states are ignored. Still the analogy of the electron configurations and the close similarities between excitation energies of A" and A' states at the FC region as

\(^7\)The maximum of the x component of the TDM belonging to $a^1A' \rightarrow b^1A'$, was obtained at C-Br=1.94 Å, while the maximum of the z component was found at C-Br=1.88 Å.

\(^8\)It is an acceptable approximation e.g. in the case of simulations along C–Br on $b^1A'$ surface or along C–Cl on $c^1A'$ surface, where the steepest gradient of the surface in the FC-region mainly points to the selected direction.
well as their degeneracy in the dissociation limit justify to consider only the A’ states. 
As shown in section 3.5, the adiabatic potential curves are formed by crossings between 
different diabatic curves. Consequently, non-adiabatic couplings at around these crossings 
may influence the dynamics and should be introduced in the Schrödinger equation. Most 
of them, however, should not influence the dynamics, since a population transfer is en-
ergetically not allowed. Hence, such effects can be safely ignored during the simulation 
of the photodissociation process in the C–Br direction after excitation to the state $b^1A'$. 
Nevertheless, in the C–Cl direction the relative small energy gap between the adiabatic 
potentials $b^1A'$ and $c^1A'$ at c.a. 1.9 Å (see Fig. 3.6) suggests that population transfer is 
possible. Thus at this point the $b^1A'$ and $c^1A'$ curves had to be diabatized. (We shall 
call the resulted potential curves semi-diabatic potentials reflecting the fact that they are 
diabatized at only one crossing while the rest of the curves are identical to the adiabatic 
one.)

First, the results of diabatization of the \textit{ab initio} potentials and TDMs according to 
Eqs. 3.16-3.18 will be presented. Then, the results of the numerical simulations will be 
discussed. For each simulation the spatial grid consisted of 2048 grid points between 
C–Cl=1.3 Å and 15 Å (for the C–Br from 1.5 Å to 15 Å) with a time discretization of 
$\Delta t=0.02$ fs. The initial state was the vibrational ground state eigenfunction, $\Phi^{(1)}_0(Q)$, de-
determined as for the CsCl, i.e., using the Fourier grid Hamiltonian method. [46] Wavepacket 
propagations in the C–Br direction were performed only on non-coupled adiabatic potential 
curves according to Eq. 3.11. In the C–Cl direction the dynamics was investigated in 
both ways: using non-coupled adiabatic potentials (similar to the C–Br case) thus ignoring 
the effect of the crossing, and also using the semi-diabatized potential- and TDM-curves 
solving Eq. 3.17. The boundary $b$, separating the interaction domain ($Q \leq b$) from the 
asymptotic domain ($b \leq Q$) of the potentials was chosen 6 Å for both directions. This 
choice was based on investigating the purity of molecular orbitals in the ground electronic 
state as a function of the internuclear distance. Indeed, none of the first three adiabatic 
potential energy curves belonging to singlet A’ states change beyond this internuclear 
separation. Results of simulations in the limit of excitation with a weak quasi-δ-pulse will 
be presented first. Then, as a more realistic case, the dissociation following resonant one-
photon excitation by a pulse of $T=100$ fs duration (FWHM=36.4 fs in intensity) will be 
discussed. Finally a Tannor-Rice control scheme will be suggested and demonstrated by 
a two-pulse simulation in the C–Cl direction. All the quantum dynamical computations 
in the present chapter were carried out on the workstations of the Theoretische Chemie 
group of the Freie Universität Berlin using a program package developed by B. Schmidt
between 1994 and 1996. The diabatization was done using the program written by P. Saalfrank and K. Finger in 1994.

### 3.6.1 Result of diabatization

<table>
<thead>
<tr>
<th>Diabatization:</th>
<th>1st</th>
<th>2nd</th>
<th>3rd</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{23}^l$</td>
<td>0.08</td>
<td>0.11</td>
<td>0.10</td>
</tr>
<tr>
<td>$\Gamma_{23}^r$</td>
<td>0.10</td>
<td>0.15</td>
<td>0.12</td>
</tr>
<tr>
<td>$r_{23}^c$</td>
<td>1.89</td>
<td>1.92</td>
<td>1.87</td>
</tr>
<tr>
<td>$\hat{r}_{23}^c$</td>
<td>1.90</td>
<td>1.94</td>
<td>1.88</td>
</tr>
</tbody>
</table>

Table 3.7: Parameters of asymmetric Lorentzian functions used for diabatizations 1, 2 and 3. Each parameter is given in Å. (The $\hat{r}_{23}^c$ values are the real crossing points, which differ from the $r_{23}^c$ because of the asymmetric nature of Lorentzian.)

Due to the interplay of many diabatics in shapes of the adiabatic curves $b^1A'$ and $c^1A'$ the exact crossing was difficult to locate. Therefore, the stability of population dynamics with respect to the choice of diabatization parameters $r_{ij}^c$, $\Gamma_{ij}^l$ and $\Gamma_{ij}^r$ was investigated, trying three different parameter sets. The choice of these parameters was based on the diabatic potential curves matching the adiabatic ones outside the region of the crossing. Also the diabatic potentials should be as smooth as possible within the region of the crossing. The results of the three diabatizations using the parameters listed in Table 3.7 are shown in Fig. 3.10. The indices of the diabatic states are written next to the curves both before and after the crossing. Notice, that the 2nd diabatic potential curve is identical to the adiabatic state $c^1A'$ in the FC-region and not to the adiabatic state $b^1A'$! The later corresponds to the diabatic curve 3 in the FC-region. The diabatized TDM are presented in Fig. 3.11 for the first parameter set. The diagonal elements of the adiabatic TDM matrix, $\mu_{ii}^a$ were set to zero, and thus not included in the diabatization, since they do not play a role for excitations by UV or visible pulses. Also the off-diagonal elements $\mu_{23}^a$ of the adiabatic TDM matrix, coupling the two excited states in the adiabatic representation, were ignored, since the photon energies of the present investigations did not match the transition energy between the first and the second excited states.

### 3.6.2 Results of propagation following a quasi-δ-pulse excitation

First the wavepacket dynamics following the excitation by a quasi-δ-pulse is investigated in the adiabatic representation using non-coupled potentials. (This means, that Eq. 3.11 was

\[9\text{From now on } i, j = a^1A', b^1A' \text{ and } c^1A' \text{ will be used for the adiabatic states and } i, j = 1, 2 \text{ and } 3 \text{ will be used for the semi-diabatic states.}\]
CHAPTER 3. AB INITIO STUDY OF CH2BRCL DISSOCIATION

Figure 3.10: Adiabatic and diabatic potentials in the vicinity of the crossing. The upper left subfigure shows the adiabatic curves while the solid lines in the rest of the figures display the diabatic potentials for three different sets of diabatizaton parameters (see Table 3.7). The dashed line represents the potential coupling $V_{23}(Q)$ multiplied by a factor 10 for better visualization. The ground state equilibrium C–Cl distance is indicated by the vertical line.

solved with initial condition Eq. 3.31.\(^\text{10}\) The propagation of the wavepackets $\tilde{\Psi}_{ij}^{(i)}(Q,t)$ for the C–Br and C–Cl directions are displayed in Figs. 3.12 and 3.13, respectively. Remind that the upper index $(i)$ of $\tilde{\Psi}_{ij}^{(i)}(Q,t)$ denotes the state where the molecule was initially excited by the pulse. The lower index $j$ denotes the state, the wavefunction belongs to. In the present case (non-coupled adiabatic potentials) no transfer between the excited states can happen (except induced by an electric field) thus only the $j=i$ state is displayed. As shown in the figures, whether the electric field is parallel to the X or to the Z components

\(^{10}\)To verify the existence of a quasi-δ-pulse in our case we may consider a 2 fs long Lorentz pulse [114], which is short compared to the timescale of the non-adiabatic wavepacket dynamics (see later) and has a bandwidth of 0.3 eV considerably lower than the 1 eV gap between the first and second excited states involved in the present investigations.
Figure 3.11: Diabatized transition dipole moment curves for the first diabatization parameter set (see Table 3.7). The ground state equilibrium C–Cl distance is indicated by a vertical line.

Figure 3.12: Propagation of 1D wavefunctions, $|\tilde{\Psi}_{iq}(Q,t)|$, in the C-Br direction after being excited by a quasi-$\delta$-pulse to the excited state adiabatic potentials $b^1A'$ or $c^1A'$. Contributions of TDM components X and Z are displayed separately.
of the TDM vector, influences mainly the amount of transferred population but not the dynamics. The \( c^1 A' \) state is bound for both C–Br and C–Cl directions. In the C–Br coordinate the first recurrence of the wavepacket to the FC-region happens at about 400 fs after the excitation while in the C–Cl direction the recurrence time is only 340 fs. This implies that in the adiabatic approximation the wavepacket in the state \( c^1 A' \) flows out from the FC-region in the C–Cl direction faster than in the C–Br direction. It can also be seen in the figures, that the wavepackets in \( c^1 A' \) broadens faster in the C–Cl direction than in the C–Br one. This is due to the shape of the C–Cl potential curve which is more irregular than that of the C–Br one. Concerning the boundedness of the adiabatic \( c^1 A' \) potential it should be emphasized again, that the present potentials are 1 dimensional and non-relaxed ones. In order to predict the long term wavepacket dynamics one should consider the effect of geometry relaxation as well as the nonadiabatic coupling between \( c^1 A' \) and other (especially the \( d^1 A' \)) states. Nevertheless, from the point of view of controlling the dissociation with femtosecond laser pulses, we are mainly interested in the early steps of the wavepacket dynamics following the excitation, when the present
approximations are still valid.

As can be seen in Figs. 3.12a)-b) and 3.13a)-b), excitation to the $b^1A'$ adiabatic state results in a direct and fast dissociation.

The population dynamics after a quasi-δ-pulse excitation to the $b^1A'$ state is shown in Fig. 3.14. The $P_{\text{diss,}i,q}(t) / P_i$ normalized dissociation probability is displayed for $i=b^1A'$, separately for the $q=x$ and $q=z$ TDM components. Since the $x$ component of the TDM vector $\mu_{12}$ is much smaller than the $z$ component, its contribution to the dissociation is negligible. Fitting the expression Eq. 3.29 to the $z$ contributions of Figs. 3.14a) and b) results in a $t_{\text{diss}}$ of 107 fs and 126.5 fs for the dissociation in the C–Br and C–Cl directions, respectively.\(^{11}\) The fact that the dissociation in $b^1A'$ is faster in the C–Br than in the C–Cl direction confirms the observation that a resonant transition to the state $b^1A'$

\(^{11}\)The rise time parameter, $D_t$, in Eq. 3.29 was found to be 2.05 fs and 4.67 fs for the dissociation in the C–Br and C–Cl directions.
Figure 3.15: On the left hand side figures the $P$ stands for the normalized excited state populations $\frac{P_{i\text{q}}^{(i)}(t)}{P_{i\text{q}}^{(i)}(\delta t)}$ for the three different diabatizations (see Table 3.7 and Fig. 3.10). The corresponding probability of dissociation, $P_{\text{diss}}$ (summarized over both the TDM components and the excited states) on the right hand side figures, stands for $\frac{P_{\text{diss}}^{(i)}(t)}{P^{(i)}}$. The initial conditions $i=2$ or $3$ are denoted in the figures by $1 \rightarrow 2$ and $1 \rightarrow 3$, respectively.

will preferentially result in the CH$_2$BrCl $\rightarrow$ CH$_2$Cl + Br reaction.
The population dynamics in the C−Cl direction on coupled semi-diabatic excited state potentials, 2 and 3 are presented in Fig. 3.15. The three pairs of subfigures belong to the three different diabatizations of the adiabatic \( b^1A' \) and \( c^1A' \) curves according to the parameters, given in Table 3.7. On the left hand side panels of Fig. 3.15, the normalized excited state population, \( \frac{P_{iq}^{(i)}(t)}{P_{iq}^{(i)}(\delta t)} \) of the initially populated diabatic state \( i \) are displayed for both excited states \( i = 2, 3 \) and TDM components \( q = x, z \). The effect of population transfer from one diabatic state to the other through the crossing is clearly seen in the figures: this is the reason for the decrease of the population in the initially populated excited state. The small irregularity at the beginning of each curve (pronounced for times less than 10 fs) is in fact a fast oscillation\(^\text{12}\) of the population between the diabatic states. Such an oscillation should not be expected provided the population is smoothly transferred from the ground to the excited state by an electric field of finite duration instead of ‘suddenly’ put to one of the diabatic potentials. On the right hand side panels of Fig. 3.15 the time dependent probability of dissociation, normalized by the total excited population \( \frac{P_{diss}^{(i)}(t)}{P^{(i)}} \) is depicted. Apart from small differences, the results for all the three diabatizations are the same. Populating the lower lying diabatic state 3 is followed by an almost complete population transfer to the dissociative diabatic state 2, i.e., more than 90% of the excited state population will be transferred within ca. 50 fs. This population is then completely dissociates as shown by the right hand side figures. Fitting the expression 3.29 again to the \( \frac{P_{diss}^{(i)}(t)}{P^{(i)}} \) curve we obtain a dissociation time, \( t_{diss} \) of 127 fs for all the three diabatizations.

Along the C−Cl coordinate, the most relevant fact is the population dynamics after exciting the molecule to the diabatic state 2, corresponding to \( c^1A' \) before the crossing. As shown in Fig. 3.15, roughly 20% of the total initial population of diabatic state 2 will only remain in this diabatic state and undergo dissociation, while the 80% will be transferred to state 3 within less than 20 fs and be trapped at least for some hundreds of femtoseconds. The fraction of population directly transferred to diabatic state 2 will be dissociated in \( t_{diss}=96 \) fs.

The fact, that the features of the population dynamics hardly depend on the diabatization parameters, allow us to restrict the further investigations to one of the three sets of diabatic potential curves. Thus in the next sections only the potentials obtained by the first diabatization will be used for simulations in the C−Cl direction.

\(^\text{12}\)The sampling of the data points was not fine enough to smoothly resolve this oscillation.
3.6.3 Results of propagation following real-pulse excitation

In order to test the dynamics in a more realistic case than the quasi-δ-pulse excitation, resonant one-photon transitions with a pulse of finite duration were also simulated. The photon energies were either 6.12 eV or 7.17 eV according to the transition energies of the \( a^1A' \rightarrow b^1A' \) and \( a^1A' \rightarrow c^1A' \) transitions. The rest of the pulse parameters were \( T=100 \text{ fs} \) (FWHM=36.4 fs in intensity), \( t_0=50 \text{ fs} \) and \( E_0=0.5 \text{ GV/m} \) (0.033 TW/cm\(^2\) peak intensity). These parameters were chosen somewhat arbitrary under the conditions that the duration of the pulse is shorter than the dissociation times obtained by the quasi-δ-pulse simulations and the pulse energy is far below the saturation energy. Again, simulations were performed using the non-coupled adiabatic potentials for the C–Br and the coupled semi-diabatic potentials (from diabatization 1) for the C–Cl direction.

The wavepacket motion along the C–Cl direction is displayed in Figs. 3.16 and 3.17 for photon energies of 7.17 eV and 6.12 eV, respectively. The wavepacket-motions resulted from different TDM components are very similar for both photon energies. Only for the 6.12 eV excitation the magnitude of the populations excited with different TDM components differs in an order of magnitude.

![Wavefunction plots](image)

Figure 3.16: Propagation of 1D wavefunctions, \(|\tilde{\Psi}_{jq}(Q,t)|\), in the C-Cl direction on diabatic potential curves \( j=2, 3 \) for the TDM component \( q=Z, X \) after being excited by a pulse of \( T=100 \text{ fs} \) duration and photon energy of 7.17 eV.
Figure 3.17: Propagation of 1D wavefunctions, $|\tilde{\Psi}_{jq}(Q,t)|$, in the C-Cl direction on diabatic potential curves $j=2, 3$ for the TDM component $q=Z, X$ after being excited by a pulse of $T=100$ fs duration and photon energy of 6.12 eV. As seen, the wavepacket obtained for the $q=X$ is very similar to that of the $q=Z$ case but an order of magnitude smaller.

The population dynamics for the first 250 fs are shown in Figs. 3.18 and 3.19 for the C–Br and C–Cl directions, respectively. Specifically, the excited state populations, $P_j(t)$ and dissociation probabilities, $P_{\text{diss},j}(t)$ are displayed, both normalized with $N$, which is the asymptotic value of the total excited state population at $t=250$ fs. For C–Br the $N = P_{b^1A'} + P_{e^1A'}$ and for C–Cl the $N = P_2 + P_3$. As seen in Fig. 3.18 the excitations are selective with both photon-energies. Fitting the expression 3.29 to the nonzero $P_{\text{diss},j}(t)/N$ components and taking into account the center of the laser pulse at $t_0=50$ fs, the following dissociation times are obtained: $t_{\text{diss}}=105$ fs for the C–Br dissociation in state $b^1A'$ in case of 6.12 eV photon energy, and $t_{\text{diss}}=130$ fs and 94.5 fs for dissociation in the C–Cl direction following the excitations by photons of energies 6.12 eV and 7.17 eV, respectively. All these dissociation times are in good agreement with those obtained from the previous, quasi-δ-pulse simulations. The rise-time $D\tau$ of the total excited state populations, $P_2 + P_3$, is always the same and is determined exclusively by the length of the pulse, as expected for a weak field excitation.
CHAPTER 3. AB INITIO STUDY OF CH$_2$BRCL DISSOCIATION

Figure 3.18: 1D population dynamics in the C–Br direction on adiabatic potentials $b^1A'$ and $c^1A'$ induced by resonant one-photon excitation. The $P$ stands for normalized excited state population, $P_j(t)/\overline{N}$, where $\overline{N}$ is the asymptotic total excited state population (for details see text). The $P_{diss}$ denotes the normalized probability of dissociation, $P_{diss,j}(t)/\overline{N}$. The photon energies are given in the figure. The pulse duration was the same, in both cases $T = 100$ fs (FWHM = 36.4 fs in intensity) and the pulse was centered at 50 fs.

Figure 3.19: 1D population dynamics in the C–Cl direction on diabatic potentials induced by resonant one-photon excitation. As for Fig. 3.18, the $P$ and the $P_{diss}$ stand for normalized excited state population, $P_j(t)/\overline{N}$ and for normalized probability of dissociation, $P_{diss,j}(t)/\overline{N}$, respectively. Photon energies are given in the figure. Pulse parameters are the same as for Fig. 3.18.
3.7 Two pulse excitation: the proposed control scheme

Under the assumption that the wavepacket in the \( c^1A' \) state moves preferentially in the C–Cl direction a Tannor-Rice control strategy can be planned for dissociating the stronger bond, C–Cl while keeping the weaker one, C–Br. This assumption is plausible since the \( c^1A' \) potential is steeper and the reduced mass is slightly smaller for the one dimensional C–Cl motion than for the one dimensional C–Br motion. Utilizing the large TDM component at around C–Cl=3 Å, a pumping from the ground state \( a^1A' \) to \( c^1A' \) and a subsequent efficient depumping back to \( a^1A' \) may lead to a selective fission of the C–Cl bond. Since the TDM values for the \( c^1A' \rightarrow a^1A' \) transition takes its maximum at an internuclear distance of about 3 Å, where the ground state potential curve has not yet achieved its asymptotic value, it is important that the kinetic energy of the depumped wavepacket is large enough to ensure the dissociation. As a demonstration of this control idea a simulation in the C–Cl direction was performed with two pulses. (The diabatic curves belonging to the first parameter set of Table 3.7 were used.) The parameters of the first pulse were the same as before, i.e., \( E_0 = 0.5 \) GV/m (0.033 TW/cm\(^2\)), \( \hbar \omega = 7.17 \) eV, \( T = 100 \) fs and \( t_0 = 50 \) fs.\(^{13}\) The parameters of the dump-pulse were \( E_0 = 2 \) GV/m, \( \hbar \omega = 3.4 \) eV \( T = 250 \) fs and \( t_0 = 125 \) fs. These parameters were chosen to get an efficient depumping. The results are presented in Fig. 3.20. The classical orientation averaging was performed for the pumping process but it was ignored for the depumping, considering that the excited molecules exhibit already an inhomogeneous orientational distribution. The populations and dissociation probabilities were normalized with the same \( \overline{N} \) value, which was used previously in case of Figs. 3.18 and 3.19, i.e., the sum of the asymptotic populations in diabatic states 2 and 3 in the absence of the depumping pulse. The effect of the second pulse is clear if we compare Fig. 3.20 and Fig. 3.19b). As a consequence of the second, more intense pulse, the excited state population \( P_3 \) starts to decrease at about 80 fs due to the depumping to the ground state. The depumped population dissociates at about 350 fs in the ground state, as indicated by the increase of \( P_{\text{diss,1}} \).

The efficiency of the control may be enhanced by utilizing the differences between the directions of transition dipole moment vector, \( \mu_{13} \) along the C–Cl and C–Br bond stretchings. The molecule at its equilibrium geometry has a dipole moment of \( \mu_{11} = [-0.62, 0, -2.14] \) au in the ground electronic state. Thus it can be aligned in a constant electric field in a way, that the C–Br axis (z axis) is roughly parallel to the direction

\(^{13}\)Taking into account the uniform initial orientational distribution of the molecules, this pulse was found to be able to excite ca. 0.5% of the initial ground state population.
of the constant electric field. Using a pump laser pulse linearly polarized perpendicular to the constant electric field, one can selectively excite those molecules, whose Br-C-Cl plane is parallel to the polarization of the laser pulse, i.e., the transition will be governed mainly by the x component of the TDM vector, \( \mu_{13} \). Concerning the depumping and subsequent dissociation, we may consider two competing dissociation channels: dissociation in the C–Br and dissociation in the C–Cl direction. Using the same x-polarization of the dump-pulse as was used for the pump-pulse again the x component of the \( \mu_{13} \) will mainly govern the transition for both stretchings. As seen in Figs. 3.8b) and 3.9b) the x component of the \( \mu_{13} \) in the C–Cl direction considerably overcomes the x component of \( \mu_{13} \) in the C–Br direction. This suggests that the depumping by an x-polarized dump-pulse should be more efficient for the C–Cl stretching than for the C–Br one.

### 3.8 Conclusion and future plans

In the present chapter the photodissociation dynamics of the CBM molecule was investigated by ab initio quantum chemical computations and numerical dynamical simulations. First the vertical spectrum was computed at the MS-CASPT2 level of theory for singlet states of both A’ and A” symmetries. Electron configurations, excitation energies and oscillator strengths were obtained. The lowest two excited states were found to have an \( n(X) \rightarrow \sigma^*(C–X) \) character for both symmetries, with \( X = \text{Br} \) being the first excited state within a certain symmetry and \( X = \text{Cl} \) was found to characterize the second excited state within the same symmetry. The lowest 202 nm resonance excitation wavelength obtained from the computation agrees well with the experimental findings. [27] The res-
onance wavelength of the second excited states was predicted at 173 nm. The vertical spectra for the dissociated states (C−X=50 Å) were also computed and compared to experimental as well as to other computational data from the literature. The agreement was satisfactory. As a next step, one dimensional non-relaxed potential energy curves were calculated for both carbon-halogen bonds for the three lowest singlet electronic states of A’ symmetry. Corresponding transition dipole vectors as a function of the bond length were also computed. The dissociation dynamics following resonant excitations with photon energies of 6.12 eV and 7.17 eV were investigated with preliminary one dimensional wavepacket propagations. The dissociation time from the lower excited state was found to be 107 fs in the C−Br direction, c.a. 20 fs smaller than in the C−Cl direction in agreement with the observations, that the dissociation from this state mainly proceeds in the C−Br direction. From the second singlet excited state (of symmetry A’) the molecule is able to dissociate via non-adiabatic coupling with the lower excited state. It was found that c.a 20% of the excited population dissociates through the crossing in the C−Cl direction within a time interval of about 96 fs. These results are, nevertheless, only preliminary, since the dynamics should be performed 2 dimensional on both surfaces. Computation of the surfaces in 2 dimensions is in progress. Computation of potential curves (or even surfaces) belonging to electronic states of A” symmetry are also planned. In the present work it was assumed, that the dynamics on the A” surfaces is very similar to the A’ ones which is not necessarily the case. Since dissociation initiated by longer wavelengths (248 nm and 265 nm) reported in the literature may take place through triplet states, the effect of spin-orbit couplings to the dissociation dynamics may be worth to consider. Success of recent experiments [10] on the CBM molecule in selectively controlling the dissociation of the halogen atoms with feedback optimized phase-modulated femtosecond pulses of 400 nm and 800 nm set up a further challenge to theoretical investigations.
Chapter 4

Summary

In the present work the dissociation dynamics of two different molecules (CsCl and CH₂BrCl) were investigated. The motivation was the same in both cases: to reveal the possibilities of controlling the dissociation by femtosecond laser pulses. The particular task in the case of the CsCl molecule was to explain the underlying mechanism of the measured pump-probe signal, whereas in the second case the emphasis was laid on computing relevant molecular properties (potential energy- and transition dipole moment curves), with the help of \textit{ab initio} quantum chemical methods.

In order to describe the pump-probe experiment on CsCl performed by A. Glaß [23, 24], a four-level model of the CsCl molecule was proposed using model potentials relevant to the photon energies applied in this experiment. The potential-parameters as well as the transition dipole moments were determined from measured spectroscopic data taken from the literature. To perform simulations of photoionization process in a more efficient way, a non-reflecting boundary condition method, already successfully used for other numerical problems, was applied here for the first time and was tested numerically.[52] Then the pump-probe experiment on the CsCl was simulated with the proposed model system. The computed pump-probe signal was found to be in a good agreement with the measured signal. This agreement may also be regarded as a verification of those assumptions that were necessarily made concerning the shape of the unknown potential curve.

As the main result, the simulations gave an explanation of the measured pump-probe signal. It was found, that the resonant depumping and the enhanced ionization efficiency at the optimal delay are strongly related. This finding served as a basis for the coherent control of the photodissociation process. The feedback-controlled optimization experiment using self-learning algorithms was then successfully performed by A. Glaß and co-workers for the first time in the strong response regime.[23, 25]
In the second part of the present work, the photodissociation dynamics of the \( \text{CH}_2\text{BrCl} \) molecule was investigated by \textit{ab initio} and subsequent quantum dynamical studies. Because of the presence of Rydberg states and of the several avoided crossings along the reaction path, it was mandatory to use a sophisticated multiconfigurational method, which can treat near degeneracies and Rydberg-valence mixing adequately. Hence all the \textit{ab initio} computations were performed with the MS-CASPT2 method being the "state-of-the-art" method concerning excited electronic states.

Using this technique, the vertical excitation energies and corresponding electron configurations and oscillator strengths were computed for 10 singlet electronic states for both \( \text{A}' \) and \( \text{A}'' \) symmetries in the equilibrium geometry of \( \text{CH}_2\text{BrCl} \) for the first time. \footnote{Ab initio computed vertical excitation energies and oscillator strengths for the \( \text{CH}_2\text{Br} \) and \( \text{CH}_2\text{Cl} \) radicals were already available in the literature. They were, however, computed here for the first time with the MS-CASPT2 method. As expected, in each case when experimental values were also available in the literature, the present MS-CASPT2 results (excitation energies, oscillator strengths) were found to fit better to the measured values than the previous theoretical results.}

As a next step one dimensional non-relaxed potential energy curves and corresponding transition dipole moment curves were determined in both the \( \text{C}−\text{Br} \) and the \( \text{C}−\text{Cl} \) directions for the lowest three singlet electronic states of symmetry \( \text{A}' \). These are the first potential curves for a \( \text{CH}_2\text{XY} \) type dihalomethane molecule computed at a sufficiently high level of theory (MS-CASPT2) being able to handle valence-Rydberg mixing and curve crossing. Furthermore, analyzing the electronic structure of the excited states, it was determined, which diabatic states contribute to the lowest two singlet adiabatic excited states, \( b^1\text{A}' \) and \( c^1\text{A}' \). The only crossing playing an important role in the dissociation dynamics (on the timescale investigated) was diabatized. Preliminary wavepacket propagations were then performed on the first two excited states and dissociation times were estimated. \footnote{Finally, based on the present \textit{ab initio} results and the subsequent wavepacket simulations and as an alternative to the control method, applied in Ref. [10], a Tannor-Rice control scheme was proposed to achieve selective fission of the stronger carbon-halogen bond of \( \text{CH}_2\text{BrCl} \) with respect to the weaker one in the neutral dissociation channel.}
Bibliography


Chapter 5

Appendix A

5.1 Comparison of two-photon ionisation process computed analytically and numerically

As discussed in section 2.4.2 if the delay time between the UV and the subsequent VIS pulses is large enough, the ground state X of the CsCl molecule does not play a role in the interaction between the VIS pulse and the (rather dissociated) molecule. In this case the ionisation from state A by the VIS pulse is equivalent to the two-photon-ionization of the neutral Cs atom from its ground electronic state. Knowing the photoionisation cross-section, \( \sigma^{(2)}_1 \) for this process, one can analytically compute the efficiency of the ionization for the given VIS pulse using a simple rate-equation model. A comparison between the efficiency computed in this way and the efficiency obtained from the numerical simulation at large delay time (500 fs) serves as a check of the implemented numerical algorithm. This comparison is done here. The following rate equations govern the population transfer:

\[
\frac{dN_A(t)}{dt} = -\frac{dN_C(t)}{dt} = -N_A(t)P_1^{(2)}(t) \tag{5.1}
\]

where \( N_A(t), N_C(t) \) denote the populations in initial state A and continuum state C and \( P_1^{(2)}(t) \) denotes the transition probability at time \( t \). This later is determined as \( P_1^{(2)}(t) = \sigma^{(2)}_1(I(t)/\hbar \omega_0)^2 \), where \( \omega_0 \) is the central frequency of the pulse belonging to the wavelength of 497 nm and \( I(t) \) is the Gaussian temporal intensity profile of the VIS laser pulse used in the simulation. The solution of Eq. 5.1 for population \( N_A(t) \) is

\[
N_A(t) = N_A(-\infty) \exp \left\{ -\int_{-\infty}^{t} P_1^{(2)}(t') dt' \right\} \tag{5.2}
\]
It is then the final ratio of the populations in state A and C to be determined. Using the same values as in the simulation\(^1\), the asymptotic ratio, \(N_C(\infty)/N_A(\infty)=0.265\) is obtained from the analytic model. By the evaluation of the results of the simulation, one should consider the small amount of continuum population resulted by the UV pulse alone already before the VIS one. Subtracting this small amount from the final continuum population, an \(N_C(\infty)/N_A(\infty)=0.240\) is obtained from the simulation. The difference is less then 10\%, which is quite acceptable and probably due to the error introduced by the approximate non-reflecting boundary condition in the numerical treatment of the ionisation process.

### 5.2 Estimation of oscillator strengths from measured spectra

Here we estimate the oscillator strengths for the lowest singlet transitions appearing in the UV spectra of the CH\(_2\)BrCl (CBM) molecule and of the free radicals CH\(_2\)Cl and CH\(_2\)Br.

\(1\sigma^{(2)} = 2.6 \cdot 10^{-50} \text{ cm}^4 \text{s} \) [68], FWHM=86 fs, peak intensity, \(I_0 = 4.7 \text{ TW/cm}^2\)

Figure 5.1: UV spectrum of CBM and its fragments. The symbols denote absorption cross sections measured by Orkin et. al. [27] for the CBM, Villenave and Lesclaux [113] for the CH\(_2\)Br radical and by Roussel et. al. [112] for the CH\(_2\)Cl. The solid line represents a fit to the results. In each case a Gaussian function was fitted to the measured values in the frequency domain.
CH$_2$Br in order to compare with the quantum *ab initio* computed values. The absorption spectrum of CBM was measured by Orkin et al. at 295 K [27]. The spectrum of the CH$_2$Cl radical was measured by Roussel et al. [112] at the same temperature while the spectrum of the CH$_2$Br radical was detected by Villenave and Lesclaux at 298 K. [113] As an approximation, the effect of line-broadening at room temperature is neglected. From the measured UV absorption cross-sections $\sigma(\lambda)$, the oscillator strength, $f$ can then be estimated as [55]

$$f = \frac{1}{\pi r_e} \int \frac{\sigma(\lambda)}{\lambda^2} d\lambda$$ (5.3)

where $r_e$ is the classical electron radius ($r_e=2.818\times10^{-6}$ nm). In each case a simple Gaussian function was fitted to the measured absorption cross sections in the energy domains. Fig. 5.1 shows the measured absorption cross sections together with the fitted curve (transformed back to the wavelength range). Theformer is shown by the symbols, the later is by the solid lines. The resulted values for $f$ are 0.0126, 0.0852 and 0.0491 for the CBM, CH$_2$Cl, and CH$_2$Br, respectively. It should be noted, that in the case of CH$_2$Cl the lack of the data (especially the short wavelength tail of the spectrum) likely resulted in an overestimation of the oscillator strength.
Chapter 6

Appendix B

6.1 Time-resolved x-ray diffraction in a molecular crystal

Although the application of femtosecond optical pulses opened a new way of exploring and controlling chemical reactions, optical probing provides only indirect information about a chemical process.\footnote{In order to evaluate the signal obtained using an optical probe pulse, one should know the potential energy surfaces.} Therefore experimental techniques, that are able to deliver direct information about the atomic motion are highly appreciated. Recent achievements in producing ultrashort Röntgen pulses [115, 116] offers a unique tool for a direct real-time measuring of the motion of the nuclei via time-resolved x-ray diffraction. [117]

Although such a measurement is not related to the goals of the previous chapters, its importance concerning the detection of coherent molecular dynamics, makes reasonable to study the theoretical aspects of a pump-probe x-ray diffraction experiment in the present appendix. The emphasis will be laid here on computing the time resolved scattering intensity for different experimental parameters.

6.1.1 Overview

The particular goal of the experiment considered below would be to monitor coherent intramolecular motion in a molecular crystal, induced by an ultrashort laser pulse on a timescale shorter than the thermalization time of the energy, i.e., in a timescale less then a picosecond. A simple model for the atomic motion will be used to reveal the possibilities
of such an experiment. As a suitable candidate, iodine molecule crystal will be considered. It has been shown experimentally for I$_2$ both in gas-phase and condensed phase (in noble-gas matrix), that large amplitude coherent vibrations, persisting several hundreds of femtoseconds can be induced by excitation at around 520 nm. [118] Moreover, theoretical investigations with time-resolved x-ray diffraction in iodine in the gas-phase [119, 120] as well as in solution [121] were performed showing the experimental possibilities in these phases. Nevertheless, no investigations in the crystal phase has been carried out yet. In Fig.6.1 the experimental idea in crystal phase is displayed schematically. A thin layer of the molecular crystal is put to a substrate. It is assumed that the diffraction pattern of the molecule crystal and that of the substrate is spatially well separated. The layer is irradiated by the femtosecond visible (VIS) pump pulse, which resonantly excites the molecules within the layer to an electronic excited state, where they exhibit large amplitude coherent intramolecular vibration. The substrate is considered to be transparent with respect to the VIS light. It is assumed that the pumping process is uniform within the whole crystal layer and the attenuation of both the VIS and X-ray intensity within the layer can be neglected. The condition for this is that the penetration depth (PD) of the VIS light into the crystal be smaller than that of the X-ray. The PD of the Cu K$_\alpha$ radiation ($\lambda=1.54$ Å, used in the forthcoming investigations) into the I$_2$ crystal is c.a. 7.1 µm for perpendicular incidence [122], whereas the PD at around $\lambda=500$ nm is in the order of 100 nm.[123] Thus the attenuation of the Cu K$_\alpha$ radiation within the excited volume can be ignored. Henceforth, choosing the thickness of the I$_2$ layer so, that it is comparable with (or even smaller than) the PD of the VIS pump pulse, both the pumping and the diffraction processes can be considered as uniform within the whole I$_2$ layer.

First the scattering cross-section and the time-resolved x-ray diffraction signal will be derived in section 6.1.2 for a molecular crystal consisting of diatomic molecules. As a next step the special case of I$_2$ molecule-crystal will be considered in section 6.1.2: the
crystal structure and the quantum-dynamical treatment of the I$_2$ molecules will be discussed. Results of computations are presented in section 6.1.3. The work is summarized in the last section. The computations presented below were performed in the LabView 5.1 environment from National Instruments.

6.1.2 Theoretical considerations

We consider a perfect crystal with diatomic molecules in the lattice points. As a major approximation real lattice vibrations will be ignored and it will be assumed that each molecule is frozen in the lattice in a way, that the only degree of freedom allowed for the motion of the nuclei is a vibration along the molecular axis. This motion is then governed by the one-dimensional time-dependent Schrödinger equation (TDSE). The wavefunction of the system will be built from the one-dimensional wavefunctions of the individual molecules. Interaction between the molecules are taken into consideration with the help of a caging potential added to the one-dimensional Hamiltonian of the individual molecules. The interaction of the molecules with the VIS pump pulse is treated in the same way as in chapters 2 and 3, i.e., in the dipole approximation. As usual the femtosecond VIS pump pulse is considered linearly polarized.

Time-resolved X-ray diffraction in crystal

The differential cross-section of the X-ray scattering is given as [124]

$$
\frac{d\sigma}{d\Omega} = \left( \frac{e^2}{m_e c^2} \right)^2 (\epsilon_k \epsilon_{k_0})^2 \left| \left\langle f \left| \sum_e \exp(iK \cdot r_e) \right| i \right\rangle \right|^2
$$

(6.1)

where $|i\rangle$ and $|f\rangle$ are the total wavefunctions of the system before- and after the scattering, respectively. The $\epsilon_{k_0}$ and $\epsilon_k$ are the polarization vectors of the incident and scattered X-ray, respectively. The $K = k - k_0$ is the difference between the wavevectors of the scattered and incident waves. The $r_e$ points to the $e$th particle (electron). Let us assume that electron $e$ belongs exclusively to molecule $\gamma$ in unit cell $j$. The position vector $r_e$ of this electron may then be expressed as

$$
r_e = R_j + R_\gamma + r_{e\gamma}
$$

(6.2)

where $R_j$ points to the origin of the $j$th unit cell in the laboratory-fixed coordinate-system, $R_\gamma$ points further to the center of mass of molecule $\gamma$ within this unit cell and $r_{e\gamma}$ points to electron $e$ of molecule $\gamma$ in the coordinate-system fixed to the molecule $(j, \gamma)$ as indicated
in Fig. 6.2. Let us introduce the notation \( \mathcal{L}_{j\gamma} = \{ L_{j\gamma}^1, ..., L_{j\gamma}^N \} \), where \( N \) is the number of the electrons in the molecule.

In case of elastic x-ray scattering the initial wavefunction \( |i\rangle \), before- and the final wavefunction \( |f\rangle \) after the scattering should be the same. Applying the Born-Oppenheimer approximation they can be written as

\[
|i\rangle = |f\rangle = \prod_{j, \gamma} \sum_{n=0}^1 \Theta_n^{j\gamma}(\mathcal{L}_{j\gamma}) \Psi_n^{n, \nu_0}(u_{\gamma}, t) \tag{6.3}
\]

where \( \Psi_n^{n, \nu_0}(u_{\gamma}, t) \) is the nuclear wavefunction of molecule \( \gamma \) in unit cell \( j \) in electronic state \( n \) and \( \Theta_n^{j\gamma}(\mathcal{L}_{j\gamma}) \) is the \( n \)th electronic eigenfunction of this molecule (with the usual parametric dependence on the internuclear distance \( u_{\gamma} \)). The \( \nu_0 \) is used to denote that the molecules were initially (i.e., before the interaction with the VIS pulse) in vibrational level \( \nu_0 \) of the ground electronic state. The following relations are true for \( \Theta_n^{j\gamma}(\mathcal{L}_{j\gamma}) \) and \( \Psi_n^{n, \nu_0}(u_{\gamma}, t) \):

\[
\langle \Theta_n^{j\gamma}|\Theta_m^{j\gamma}\rangle = \delta_{n,m} \tag{6.4}
\]

and

\[
\sum_{n=0}^1 \langle \Psi_n^{n, \nu_0}(t)|\Psi_{n, \nu_0}(t)\rangle = 1 \tag{6.5}
\]

for all \( j \) and \( \gamma \) for all time \( t \). Now we can evaluate Eq. 6.1. Substituting Eq. 6.3 into it, the last term on the l.h.s will reduce to

\[
\langle f|\sum_{i} \exp(iK_{i}\mathcal{L}_{i})|i\rangle = \sum_{j, \gamma} \exp\{iK_{j}(R_{j} + R_{\gamma})\} \sum_{n, m} \langle \Psi_{n, \nu_0}(t)|C_{nm}(K, u_{\gamma})|\Psi_{n, \nu_0}(t)\rangle \tag{6.6}
\]

where \( C_{nm}(K, u_{\gamma}) \) is defined as

\[
C_{nm}(K, u_{\gamma}) = \langle \Theta_n^{j\gamma}|\sum_{s}^N \exp(iK_{s}\mathcal{L}_{s})|\Theta_m^{j\gamma}\rangle \tag{6.7}
\]

where the summation for \( s \) goes over all the electrons in the molecule. For the diagonal terms \( C_{nn}(K, u_{\gamma}) \) one obtains

\[
C_{nn}(K, u_{\gamma}) = \int \rho_n(r) \exp(iK_{s}r) dr \tag{6.8}
\]

where \( \rho_n(r) \) is the charge density within the whole molecule in electronic state \( n \). For the evaluation of Eq. 6.8 the independent atom model (IAM) approximation is commonly used. \[117\]
In the IAM approximation it is assumed, that each electron exclusively belongs either to
one or to the other atom, i.e., the electron density between the atom-cores is negligible
with respect to the electron density at around the cores. The charge density \( \rho_0(r) \)
of the molecule is then approximated by the sum of the charge densities of the individual
atoms. Furthermore in a molecule, where the number of core electrons highly overcome
the number of the valence electrons, the charge density \( \rho_1(r) \) in the excited electronic
state corresponding to a one-electron excitation (such as in the case of our model system
of I\(_2\) molecule; see later) may be well approximated by the charge density, \( \rho_0(r) \) of
the ground state. Using these approximations one obtains

\[
C_{nn}(K, u_{\gamma}) = 2f(K) \cos(K u_{\gamma})
\]  

(6.9)

for a homonuclear diatomic molecule, where \( |u_{\gamma}| \) is the half of the internuclear distance
and \( f(K) \) is the usual atomic scattering factor defined for the individual atom as

\[
f(K) = \int \rho(r) \exp(iK r) dr
\]  

(6.10)

where \( \rho(r) \) is the atomic charge density. Considering Eq. 6.9 one can see, that the expression for \( C_{nn} \) can theoretically be equal to zero, provided the \( \cos(K u_{\gamma})=0 \). Hence, in
opposite to x-ray diffraction in gas- or liquid phase, in case of a perfect and cold crystal
the experimental arrangement (geometry) may be chosen in a way, that these terms vanish
for all the molecules. In this case, the role of the otherwise negligible terms is enhanced
and the approximations implicit in the IAM should be reconsidered. In the following,
we will investigate only those arrangements, where the \( C_{00} \) term has a high value. With
other words only the changes of the scattered intensity at the diffraction spots of the
unperturbed crystal are considered. \(^3\) Under this assumption, the cross-electronic terms
\( \langle \Psi_0^{n,\alpha}|C_{01}(K, u_{\gamma})|\Psi_1^{n,\alpha}\rangle \) as well as \( \langle \Psi_1^{n,\alpha}|C_{10}(K, u_{\gamma})|\Psi_0^{n,\alpha}\rangle \) can also be ignored with respect to the terms \( \langle \Psi_1^{n,\alpha}|C_{nj}(K, u_{\gamma})|\Psi_1^{n,\alpha}\rangle \). The reason for this is that the ground state
nuclear wavefunction is all the time well localized at the equilibrium internuclear distance
and thus its overlap with the excited state wavepacket is most of the time small, especially
for the model system of I\(_2\) (see the extremely different shapes of the excited and that of
the ground state potential curves in the next section). Moreover, in the case when the
ground state is well described with a Slater determinant as defined in Eq. 3.1 and the
excitation corresponds to the transfer of one electron from an occupied molecular orbital
\( \phi_{j\gamma}^o \) to an unoccupied orbital \( \phi_{j\gamma}^r \), the term \( C_{01} \) (and similarly the \( C_{10} \), too) can be written

\(^3\)This means that in our investigations the \( K \) is always equal to some inverse lattice vector, see later.
as \( C_{01}(K, u_\gamma) = \langle \phi^a_{j\gamma} | \exp(i K \mathbf{R}) | \phi^c_{j\gamma} \rangle \), thus containing only the contribution of the excited electron, which should be small compared to the terms expressed by Eq. 6.9 containing the contributions of all the electrons, provided the \( \cos(K u_\gamma) \) term is not zero for the ground state equilibrium value of \( u_\gamma \), which is fulfilled in our investigations.

Making the above approximations we can finally set up the formula for the differential scattering cross section as

\[
\frac{d\sigma_{\nu_0}}{d\Omega}(K, t) = \left( \frac{e^2}{m_c c^2} \right)^2 (\epsilon_k \epsilon_{k0})^2 \left| \sum_j \exp(i K \mathbf{R}_j) \right|^2 |F(\nu_0, K, t)|^2,
\]

(6.11)

where \( F(\nu_0, K, t) \) is the unit cell scattering factor, which we assumed to be the same for all unit cells. It is given by

\[
F(\nu_0, K, t) = F_0(\nu_0, K, t) + F_1(\nu_0, K, t),
\]

(6.12)

where

\[
F_n(\nu_0, K, t) = \sum_\gamma f(K) \exp(i K \mathbf{R}_\gamma) \langle \Psi_{\nu_0}^{n, \nu_0}(u_\gamma, t) | 2 \cos(K u_\gamma) | \Psi_{\gamma}^{n, \nu_0}(u_\gamma, t) \rangle,
\]

(6.13)

For unpolarized X-ray one should average the \( (\epsilon_k \epsilon_{k0})^2 \) term in Eq. 6.11 over the polarization directions which results for scattering angle \( \theta \) in

\[
\langle \epsilon_k \epsilon_{k0} \rangle^2 = \frac{1}{2} (1 + \cos^2 \theta).
\]

(6.14)

To account for the distribution of the molecules among different vibrational states as initial wavefunctions, it is assumed, that the molecules are in thermal equilibrium in the ground electronic state before the interaction with the VIS pulse. Hence an averaging over the distribution of the initial vibrational states is also required. Thus the overall time-dependent scattering cross section can be expressed as

\[
\frac{d\sigma}{d\Omega}(K, t) = \sum_{\nu_0} P_{\nu_0}(T) \frac{d\sigma_{\nu_0}}{d\Omega}(K, t),
\]

(6.15)
Figure 6.3: Arrangement of I\(_2\) molecules in the crystal. Each molecule lays in the \(bc\) planes as displayed in Fig. 6.3. The positions of atom cores are indicated at the equilibrium positions in proportion, whereas the atoms themselves are displayed schematically by circles. The two-atomic unit cell, used in the present work, is indicated by dashed lines. The \(b\) and the \(c\) lattice vectors are indicated by dashed arrows. The small arrows along the molecular axis indicate the positions of the atoms corresponding to the maximal internuclear distance of 4.5 Å. The optimal choice of the polarization direction of the VIS pump pulse is also indicated in the figure.

where \(P_{\nu}(T)\) is the Boltzmann factor at temperature \(T\). The final pump-probe signal \(S(K, t)\) is then to be computed as

\[
S(K, t) = \int_{-\infty}^{+\infty} \frac{d\sigma}{d\Omega}(K, t') I_X(t' - t) dt'.
\]  

(6.16)

where \(I_X(t)\) is the intensity of the X-ray and now \(t\) stands for the delay between the centers of the VIS and X-ray pulses, which we both assume to have Gaussian temporal profile.

The model system: I\(_2\)

The iodine molecule crystal has an orthorhombic crystal structure with the orthogonal lattice vectors \(a' = [7.26 \text{ Å}, 0, 0]\), \(b' = [0, 4.79 \text{ Å}, 0]\) and \(c' = [0, 0, 9.79 \text{ Å}]\). The I\(_2\) molecules are grouped in layers parallel to the \(bc\) plane. The arrangement of the molecules in the plane is displayed in Fig. 6.3. The equilibrium internuclear distance of the molecules are fairly equal to the gas-phase value, \(x_1\) (see in Table 6.1). The angle \(\beta\) (cf. Fig. 6.3) between the molecular axis and the lattice vector \(b\) is 57.9°. In order to excite each molecule uniformly nevertheless in the most efficient way by a linearly polarized VIS pulse, the polarization direction should be chosen parallel to the lattice vector \(c\), as indicated in Fig. 6.3.

The diffraction process is governed by the Bragg condition, i.e., the diffraction spots can be observed in directions, for which the \(K = G\), where \(G\) is a reciprocal lattice vector defined as a linear combination of the elementary reciprocal lattice vectors \(g_i\),

\[
G = h'g_1' + k'g_2' + l'g_3'
\]  

(6.17)
where the $g'_i$ vectors are unambiguously determined by the primitive lattice vectors as

$$
g'_1 = 2\pi \frac{b' \times c'}{a'(b' \times c')} , \quad g'_2 = 2\pi \frac{c' \times a'}{a'(b' \times c')} , \quad g'_3 = 2\pi \frac{a' \times b'}{a'(b' \times c')} .
$$

(6.18)

The coefficients, $h'k'l'$, called the Miller indices and are used to assign crystal planes containing the atoms and staying perpendicular to $G$. Choosing the unit cell, i.e., the $a'$, $b'$, and $c'$ vectors, in a different way, the assignment of the crystal planes and thus that of the diffraction spots changes consequently. In the present work we have chosen a nonconventional unit cell involving atoms of only two molecules, i.e., containing the two molecules completely as indicated in Fig. 6.3 by dashed lines. The corresponding new lattice vectors are $a = [3.63 \text{ Å, } 2.395 \text{ Å, } 0]$, $b = b'$, $c = c'$. The $b$ and the $c$ lattice vectors are indicated in Fig. 6.3 by dashed arrows. The new Miller indices $hkl$ are obtained from the conventional ones as

$$
h = \frac{1}{2}(h' + k') , \quad k = k' , \quad l = l' .
$$

(6.19)

From now on, these new $hkl$ values are used to assign the diffraction spots investigated.

As mentioned in the previous section, the motion of the atoms are treated quantum-mechanically in one dimension along the molecule axis. As a crude approximation it was assumed that for moderate internuclear distances the low lying electronic states can be characterized by the same potential curves, that are given for gas phase molecules [118] and the interaction between atoms belonging to different molecules was taken into consideration only when the internuclear distance within the atoms of a molecule becomes larger than a certain value, $x_c$.

The ground electronic state of the gas phase molecule has the character of $^1\Sigma_{0+}$, while the electronic excited state, $B$, is $^3\Pi_{0+}$. [126] This state belongs to a one-electron excitation from the bounding $\pi_g$ valence orbital to the unoccupied $\sigma_u^*$ molecular orbital, both formed by $5p$ atomic orbitals. The transition dipole moment of this transition, used in the present computations, was given as $\mu=0.435$ au in Ref. [126]. Although the state $B$ crosses some other diabatic excited states in the gas-phase molecule due to the relative weak coupling, these crossings play an important role only on a timescale longer than that of the present investigations.[126, 118] Therefore these diabatic potentials are ignored here.

Both the ground- and the excited state potentials $V_0(Q)$ and $V_1(Q)$, respectively, were constructed as a sum of a Morse-potential, describing the gas-phase $I_2$ molecule [118] and a half-harmonic potential, $V_c(Q)$, standing for the caging in the crystal.

$$
V_n(Q) = D_n(1 - e^{-\beta_n(Q - x_n)})^2 + C_n + V_c(Q) ,
$$

(6.20)
The Morse-potential parameters are listed in Table 6.1 and $V_c(Q)$ is defined as

\[ V_c(Q) = \begin{cases} D_c(Q - x_c)^2 & \text{if } Q > x_c \\ 0 & \text{otherwise} \end{cases} \]  

(6.21)

The variable $Q$ is the internuclear distance, i.e., it is equal to $|2u|$. The parameters $D_c$ and $x_c$ were chosen arbitrary under the constraint that the atoms of a molecule do not apart from each other so much that any of them leaves the unit cell it belongs to, where the unit cell was chosen in a way, that a molecule at the ground state equilibrium geometry is either completely out of it or included in it (see later).

The potential curves are shown in Fig. 6.4. Solid curves display the Morse potentials, whereas the dashed lines indicate the added caging potential for parameters $D_c=100$ eV/nm$^2$ and $x_c=4.5$ Å. Using these potentials, the time-dependent Schrödinger equation for the two-level system can be written as

\[
-i\hbar \frac{\partial}{\partial t} \begin{bmatrix} \Psi_0(Q,t) \\ \Psi_1(Q,t) \end{bmatrix} = \left\{ \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial Q^2} + \begin{bmatrix} V_0(Q) & \mu \xi(t) \\ \mu \xi(t) & V_1(Q) \end{bmatrix} \right\} \begin{bmatrix} \Psi_0(Q,t) \\ \Psi_1(Q,t) \end{bmatrix} 
\]  

(6.22)

where $m$ is the reduced mass of the $I_2$ molecule.

The atomic scattering factors $f(K)$ was approximated by the following formula [127]

\[
f \left( \frac{\sin \theta'}{\lambda_X} \right) = \sum_{i=1}^{4} a_i \exp \left( -b_i \sin^2 \theta' / \lambda_X^2 \right) + c
\]  

(6.23)
where $\theta'$ is the half of the scattering angle $\theta$. The parameters $a_i, b_i$ and $c$ for the iodine atom are listed in Table 6.2.

<table>
<thead>
<tr>
<th>$a_i$</th>
<th>20.1472</th>
<th>$b_1$</th>
<th>4.3470</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_2$</td>
<td>18.9949</td>
<td>$b_2$</td>
<td>0.3814</td>
</tr>
<tr>
<td>$a_3$</td>
<td>7.5138</td>
<td>$b_3$</td>
<td>27.766</td>
</tr>
<tr>
<td>$a_4$</td>
<td>2.2735</td>
<td>$b_4$</td>
<td>66.8776</td>
</tr>
</tbody>
</table>

Table 6.2: Coefficients $a_i, b_i$ used in the formula 6.23 for computing the atomic scattering factor of iodine. The parameter $c$ in this formula is equal to 4.0712. The parameters are taken from Ref. [127]

6.1.3 Numerical results

The subjects of the present investigations were chosen from the most intense diffraction spots under the constraint that the Miller indices $k$ and $l$ are not both equal to zero at the same time. In case of $k=l=0$, the $G$ is perpendicular to the bc plane and thus to the axis of all the molecules. Hence, according to Eq. 6.8, the $C_{nn}$ becomes independent of the internuclear distance (remember, $K = G$ in the present investigations) and thus the $S(t)$ signal is constant. The allowed Miller indices and the corresponding diffracted intensities were determined according to the dynamical diffraction theory using the computer program DIXI [128]. The investigations presented here were carried out for the Cu K$\alpha$ radiation ($\lambda_X = 1.54$ Å). The most intense diffraction spots, involved in the investigations, correspond to the following $hkl$-indices: 004, 104, 112 and 123. Both the VIS and the X-ray pulses were taken to have Gaussian temporal profiles. In all the computations the wavelength and the FWHM of the VIS pump pulse are 526 nm and 85 fs, respectively and the VIS pulse is centered at time zero. The FWHM of the X-ray pulse was taken either 75 or 150 fs.

As is seen from Eqs. 6.11 and 6.16 the temporal changes of the x-ray signal $S(t)$ is determined by the time-evolution of the UCSF, which reflects the coherent vibration of the excited state wavepacket. This vibration may be influenced by the caging effect, thus the dependence of the UCSF on the caging potential parameters was first investigated. Since choosing larger $D_c$ or choosing smaller $x_c$ should have similar effects, only the dependence on $x_c$ is discussed here. The $D_c$ was chosen as 100 eV/nm$^2$ for all the computations. The time-evolution of the UCSF components in case of different $x_c$ parameters is presented.

$^4$As long as the condition $K = G$ is fulfilled, the choice of a different $\lambda_X$ implies a considerable change only in the diffraction angle but not in the temporal shape of the diffracted signal.
in Fig. 6.5 for the hkl=004 arrangement. Panels a), b), c), d) and e) display the excited state UCSF component, $F_1$ for $x_c=5.0, 4.5, 4.0, 3.5$ and $3.0$ Å, respectively, whereas panel f) shows the ground state component $F_0$, which is practically independent of the caging potential parameters.

Figure 6.5: Components $F_1(\nu_0, K, t)$ and $F_0(\nu_0, K, t)$ of the unit cell scattering factor for different caging potential parameters, $x_c$ for $\nu_0=0, ..., 3$. The corresponding $\nu_0$ are indicated next to the curves. The pump pulse parameters are $\lambda=526$ nm, FWHM=85 fs, $I_0=3.0$ TW/cm$^2$. The Miller indices are hkl=004 for each case. The wavelength of the X-ray is 1.54 Å corresponding to the Cu Kα radiation. Panels a), b), c), d) and e) show $F_1(\nu_0, K, t)$ for $x_c=5.0, 4.5, 4.0, 3.5$ and $3.0$ Å, while panel f) displays $F_0(\nu_0, K, t)$ for $x_c=3.0$ Å.
Figure 6.6: Time-resolved X-ray diffraction signal for different $x_c$ caging potential parameters. Panels a) and b) correspond to $T=100$ K and $300$ K, respectively. The $x_c$ parameter values are displayed next to the curves in Å. The Miller indices are 004 for each case. The FHWM of the X-ray pulse is 75 fs. All the other parameters are the same as for Fig. 6.5.

potential parameters. Four curves are presented on each subfigure belonging to the first four vibrational eigenfunctions of the ground electronic state as initial wavefunctions. The corresponding quantum-numbers $\nu_0$ are indicated next to the curves.

As we see, the excited-state UCSF components $F_1$ reflects the periodic motion of the excited state wavepacket, whereas the ground state UCSF component $F_0$ is practically constant after the VIS pulse is ceased. The decrease of $|F_0|$ during the presence of the pump pulse is due to the decrease of the ground state population. Since the Franck-Condon factor is different for different vibrational eigenfunctions, the amount of the excited population and thus the final value of $F_0$ is different for different initial vibrational states.

On the other hand, the higher the $\nu_0$, the longer the wavepacket can propagate towards larger internuclear distances in the excited state. As a consequence, caging potentials with larger $x_c$ affect only the motions of the excited state wavepacket generated from higher vibrational eigenfunctions. This effect is clear in Fig. 6.5: The decrease of $x_c$ from 5 Å to 4.5 Å influences only the $F_1(\nu_0=3, K, t)$, while the $F_1(\nu_0 < 3, K, t)$ terms are only influenced by a further decrease of $x_c$ from 4.5 Å to 4.0 Å. Nevertheless higher vibrational states are populated only at higher temperatures and thus at room temperature the signal $S(t)$ is determined mainly by the $F_0(\nu_0=0, K, t)$ and $F_1(\nu_0=0, K, t)$ as can be seen in Fig. 6.6. Figs. 6.6a) and b) display the time-resolved x-ray diffraction signals $S(t)$ for different $x_c$ parameters (indicated next to the curves in Å) at temperatures of 100 and 300 K, respectively. The period of the oscillation directly reflects the period of the coherent vibrations in the excited state. During the pumping process, the excited state
wavepacket resides in the FC-region and the fast decrease of $F_1$ at around time zero only compensates the increase of $F_0$. As soon as the VIS intensity starts decreasing, the excited state wavepacket is released from the FC-region and starts moving back and forth along the internuclear distance. The time of its first recurrence to the FC-region corresponds to the second minimum of $F_1$. The smaller the $x_c$ and the smaller the $\nu_0$, the smaller is this recurrence time. (For $\nu_0 = 0$ and $x_c = 4.5$ Å, this recurrence takes place at around $t=550$ fs.) Moreover smaller $x_c$ results in a smaller spatial amplitude of the coherent vibration and thus a decrease of the amplitude of the oscillations in both the $F_1$ and in the $S(t)$ (see Fig. 6.6).

Increasing the $x_c$ beyond a critical value, the caging potential does not affect the $S(t)$ signal any more. This critical value is temperature dependent and seems to be ca. 4.2 Å at 100 K. In the following investigations the $x_c = 4.5$ Å will be used.

Figure 6.7: Components $F_0(\nu_0, K, t)$ and $F_1(\nu_0, K, t)$ of the unit cell scattering factor are displayed in panels a) and b), respectively. The Miller indices are hkl=123. All the other parameters are the same as for Fig. 6.5b), i.e., $x_c = 4.5$ Å.

All the results presented so far, were obtained for the hkl=004 arrangement. Fig. 6.7 displays the UCSF components for a different arrangement, namely for hkl=123. The small oscillation in $F_0(t)$ seen in Fig. 6.8a) is due to the fact that the wavepacket remaining in the ground excited state after the excitation is no more an eigenfunction of the ground electronic state, hence it vibrates too, although with much smaller amplitude than the excited state wavepacket. Since this oscillation is less pronounced for $\nu_0 = 0$ than for the higher vibrational eigenfunctions, it does not influence the diffraction signal. Nevertheless, two major differences are also seen in Fig. 6.7 compared to the Fig. 6.5: i) the signs of the UCSF components are reversed and ii) the $F_1$ components are more sharply peaked at around the recurrence times. The first one does not influence the signal, whereas,
Figure 6.8: Time-resolved X-ray diffraction signal $S(t)$ defined in Eq. 6.16 for Cu Kα radiation ($\lambda = 1.54 \text{ Å}$) for different experimental arrangements. The Miller indices h, k, l are indicated next to the corresponding curves. Panels a) and b) belong to FWHM_{X-ray} = 75 fs while panels c) and d) belong to FWHM_{X-ray} = 150 fs. For the left hand side panels the temperature and the peak intensity of the VIS pulse are 100 K and 3.0 TW/cm$^2$, respectively. For the right hand side panels these parameters have the values of 300 K and 0.75 TW/cm$^2$, respectively. The cage-potential parameters were $D_c=100 \text{ eV/nm}^2$ and $x_c=4.5 \text{ Å}$.

The second feature is reflected also in $S(t)$ as shown in Fig. 6.8. This figure displays the time-resolved x-ray diffraction signal $S(t)$ for all the four arrangements, investigated. The $hkl$ values are displayed next to the curves. The left hand side and the right hand side panels belong to 'favorable' and 'unfavorable' experimental situations, respectively. The 'favorable' means cold crystal (T=100 K) and high pump intensity (3.0 TW/cm$^2$ peak intensity) while the 'unfavorable' means that the crystal is at room temperature (T=300 K) and the pump pulse is relatively weak (0.75 TW/cm$^2$ peak intensity). In both cases, $S(t)$ was determined for two different x-ray pulse widths: Figs. 6.8a) and b) were computed for x-ray pulse of FWHM=75 fs, whereas Figs. 6.8c) and d) were obtained for x-ray pulse
Figure 6.9: Time-resolved X-ray signal, $S(t)$ for different pump-pulse intensities. The peak intensities of the pump pulse is written next to the curves in TW/cm$^2$. The hkl=004 and all the other parameters are the same as for Fig. 6.8.

of FWHM=150 fs.$^5$ As expected applying longer probe pulses makes the maxima of the signal less sharply peaked. The major difference between the signals belonging to the 'favorable' and to the 'unfavorable' case is the signal to background ratio. Nevertheless, even in the most unfavorable case (panel d) with long x-ray pulse, high temperature and small pump intensity) a comfortably large signal is obtained for three of the four arrangements. It should be noted, however, that the degrees of freedom of the atomic motion was reduced considerably in the present investigations. Incoherent lattice vibrations especially at higher temperatures may lead to low signal to noise ratio. The main reason for the difference in the signal to background ratio between the 'favorable' and the 'unfavorable' cases is the difference in the intensity of the VIS pump pulse as is clarified in Fig. 6.9. It presents the signal for three different peak intensities of the pump pulse, i.e., for the highest intensity 3.0 TW/cm$^2$ as well as its 75% and 25% value. The decrease of the amplitude of the oscillation, or with other words, the decrease of the signal to background ratio with decreasing pump intensity is due to the decrease of the population in the excited state.

6.1.4 Conclusion

In the present appendix the possibility of detecting coherent intramolecular vibrations in molecular crystal via a pump-probe time-resolved x-ray diffraction measurement was considered. The time-resolved diffraction signal was derived for a crude model of a crystal consisting of diatomic molecules. As a suitable candidate iodine molecule crystal was investigated. The molecular vibration was treated quantum-mechanically where the potential curves of the gas-phase molecule were adapted and extended with a simple half-harmonic potential to model the caging effect in the crystal. Diffraction signal was investigated as

$^5$Since the peak intensities of the 75 fs and 150 fs x-ray pulses were the same in the computations, the signal for the second case is twice the signal of the first one.
a function of several parameters, such as the caging potential parameter, temperature, pump-pulse intensity and the geometrical arrangement (Miller-indices). It was found, that choosing the diffraction spot properly, even in the case of the most 'unfavorable' set of the other parameters, involved in the present investigations, a clear oscillatory signal may be expected, which directly reflects the coherent vibrations in the excited state. A comparison between the frequency of the oscillatory signal in the gas-phase and in the crystal phase may serve with information about the intermolecular forces.

A disadvantage of the present detection scheme with respect to optical pump-probe technique, such as described in Ref. [118], is that a large amount of population transfer to the excited state is required for large signal to background ratio. On the other hand pump-intensity should be kept as low as possible in order to avoid damaging the crystal and multiphoton processes while the length of the pump pulse should also be short, at least considerably shorter than the vibration period in the excited state. Usage of \( \pi \) pulses and pulse shaping is thus recommended.

The major shortcoming of the present model, is its oversimplified nature relating the excited state potential surface. Future investigations should treat the atomic motion in higher dimensionality using more sophisticated excited state potentials.
Zusammenfassung

In der vorliegenden Arbeit wird die Dissoziationsdynamik von zwei verschiedenen Molekülen (CsCl und CH\textsubscript{2}BrCl) untersucht. Ziel der Untersuchungen ist, Möglichkeiten zu finden, die Dissoziation dieser Moleküle durch Anwendung von Femtosekunden-Laserpulsen zu kontrollieren. Im Fall des CsCl Moleküls soll speziell der Mechanismus geklärt werden, der zu im Experiment beobachteten Pumpe-Probe Signale führt. Im Fall des CH\textsubscript{2}BrCl Moleküls liegt der Schwerpunkt auf der Berechnung relevanter molekularer Eigenschaften (Potential- und Übergangsdipolmomentkurven) mit Hilfe von \textit{ab initio} quantenchemischen Methoden.


durchgeführt, das bezüglich angeregter Elektronenzustände als das modernste Verfahren gilt.
Mit Hilfe dieser Methode werden erstmals die vertikalen Anregungsenergien der 10 niedrigsten Singulett-Elektronenzustände des CH₂BrCl Moleküls im Gleichgewicht, sowohl für die A’ als auch für die A” Symmetrien berechnet [84]. Zusätzlich werden auch erstmalig zu diesen Zustände gehörigen Elektronenkonfigurationen und Oszillatorenstärken bestimmt [84]. Mit ab initio Verfahren berechnete vertikale Anregungsenergien und Oszillatorenstärken stehen zwar für die CH₂Br und CH₂Cl Radikale bereits in der Literatur zur Verfügung, doch werden sie hier zum ersten Mal mit der MS-CASPT2 Methode berechnet. Wie erwartet, ergeben die mit der MS-CASPT2 Methode gewonnenen Ergebnisse bessere Übereinstimmungen mit experimentellen Resultaten als die in der Literatur verfügbaren theoretischen Werte.
Danksagung

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- Prof. Dr. Gábor Szabó, der mich mit den Kontrollexperimenten an CsCl Molekülen am IOQ in Kontakt gebracht hat, Prof. Dr. Regina de Vivie-Riedle, die den richtigen Weg der numerischen Behandlung des Ionisationsprozesses gezeigt hat; Dr. Ortrud Wehrhan, die mir bei den Berechnungen der Röntgenbeugungsordnungen geholfen hat, Dr. Jürgen Full, der mir an der FU bei den quantendynamischen Programme behilflich war.

Ehrenwörtliche Erklärung

Ich erkläre hiermit ehrenwörtlich, daß ich die vorliegende Arbeit selbständig, ohne unzulässige Hilfe Dritter und ohne Benutzung anderer als der angegebenen Hilfsmittel und Literatur angefertigt habe. Die aus anderen Quellen direkt oder indirekt übernommenen Daten und Konzepte sind unter Angabe der Quelle gekennzeichnet.


Die Arbeit wurde bisher weder im In noch im Ausland in gleicher oder ähnlicher Form einer anderen Prüfungsbehörde vorgelegt.

Ich habe weder früher noch gegenwärtig die Eröffnung eines Verfahrens zum Erwerb des akademischen Grades doctor rerum naturalium an einer anderen Hochschule beantragt.

Die geltende Promotionsordnung der Physikalisch-Astronomischen Fakultät ist mir bekannt.

Ich versichere ehrenwörtlich, daß ich nach bestem Wissen die reine Wahrheit gesagt und nichts verschwiegen habe.

Jena, 01. November 2002

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Jena, 01. November 2002