Curve-crossing quantum wavepacket dynamics

- Experiment and theory

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Abstract

In this thesis, I present experimental and theoretical work on quantum wavepacket dynamics in potential curve-crossings, using gas-phase Rb$_2$ as working media. Particularly, we have focused on curve-crossing cases with intermediate strength coupling, which leads to complicated wavepacket motion with e.g. large splittings and interference. Previous experiments on such systems are scarce.

Experimentally, femto-second pump-probe spectroscopy was performed using two independent optical parametric amplifiers. A near-effusive Rb$_2$ molecular beam source was developed to produce a stable, high density and collision-free beam. Pump-probe fluorescence was detected using an optical assembly designed for good collection efficiency.

Theoretically, analysis of experimental data was aided by quantum dynamical calculations. The used numerical simulation program is powerful in its ability to include any number of states with coupling elements, together with a fully time propagated pump pulse-molecule interaction. It was further developed to include molecular rotation as a centrifugal correction term to the potential curves, and to do statistical thermal averaging to permit direct comparison with experiment.

Our work on the Rb$_2$ A-state system is a pioneering femto-second experimental curve-crossing study of a system of two intermediately coupled bound electronic states. The wavepacket fragments, following different roads, meet and interfere at their return to the crossing. Thus, new results on the interference properties of wavepacket dynamics in such a system were obtained, such as the existence of two hybrid diabatic/adiabatic trajectories, robust towards thermal averaging. Further, we show that certain scanning possibility exist between relative contents of these two trajectories at elevated temperature by scanning the pump wavelength. The system represents a quantum matter-wave close analogue to an optical pulsed Michelson interferometer. The dynamics of the A-state system was also investigated by anisotropy measurements. The high degree of signal to noise ratio obtained, revealed a new type of small oscillatory structure, which the analysis shows originates from coupling between all degrees of freedom of the Rb$_2$ molecule, namely electronic, vibrational and rotational motion.

The results of the work on the higher lying D-state system consist of the determination of a parallel excitation mechanism, where two wavepackets are simultaneously created in two different electronic states. Further analysis showed that their future dynamics proceed essentially independently. One performs adiabatic dynamics in a single ‘shelf-shaped’ state, while the other goes through curve-crossings of somewhat weaker coupling strength than intermediate. We propose the shape of the final, unknown, pump-probe states, guided by the quantum dynamical simulations together with the experimental data.
List of papers

The following papers are included in this thesis:

I. **Coherent multichannel nonadiabatic dynamics and parallel excitation pathways in the blue-violet absorption band of Rb$_2$**
   N. Gador, B. Zhang, R. Andersson, P. Johansson, T. Hansson

II. **Bound-bound state quantum wave packet dynamics in the intermediate coupling range: the $^3 \Sigma_u^+ (0_u^+)$ and $^3 \Pi_u (0_u^+)$ system in Rb$_2$**
    B. Zhang, N. Gador, T. Hansson

III. **Dynamical interference structures in strongly coupled bound-bound state quantum wavepacket dynamics**
    N. Gador, B. Zhang, H. O. Karlsson, T. Hansson
    To be submitted to Phys. Rev. A

IV. **Intramolecular wavepacket interference in transient anisotropy of strongly coupled bound-bound state system**
    N. Gador, B. Zhang, T. Hansson
    To be submitted to Phys. Rev. Lett

Papers not included in this thesis

V. **Lifetime measurements of the $^2 \Pi_{1/2}$ state of BaF using laser spectroscopy**
   L.-E. Berg, N. Gador, D. Husain, H. Ludwigs, P. Royen

VI. **Time-resolved optical double resonance spectroscopy of the $^2 \Sigma^+$ state of BaCl**
    H. Ludwigs, N. Gador, L-E. Berg, P. Royen, L. Vikor
Comments on author’s contribution

Working in a relatively small group, and operating the whole experiment, one has to know a little bit of everything. The presented papers in this thesis is a result of teamwork among the authors, technical staff and group members.

My main responsibilities of the experimental work has been the operation and development of the molecular beam machine, plus development and maintenance of the electronic setup together with the software computer control. My ‘least’ contribution has been the operation of the femto-second laser and the two optical parametric amplifiers.

On the theoretical analysis side, I have taken active part of the physical discussions among the authors, as well as performing most of the numerical simulations. I have also taken part of the development of the used models, as well as the used simulation programs. I have helped out with the writing and organisation of the papers, taking larger part for each new paper.
Acknowledgement

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1 Introduction

Working in the field of chemical physics, the ultimate goal is to increase our knowledge of chemical reactions on a most fundamental level. Molecular bond breaking and bond formation is at the heart of chemistry. In nature, most chemical reactions proceed in the liquid phase, since the density and mobility of molecules are high. The complexity of large molecule reactions and physical behaviour in a liquid environment, is challenging and interesting, but also put a large demand of good understanding of simpler systems, such as isolated gas-phase small molecule systems. The long term intention of my work, is precisely to study simple molecular systems, relevant to chemistry of more complicated systems. A most basic chemical reaction, or part of it, is the reaction $X+YZ \rightarrow XY+Z$, which may be a linear tri-atomic molecule, breaking one bond and forming a new bond. Such reactions often go via energy-barriers [1] and is schematically shown in fig 1.1, where $R$ is the inter-nuclear distance.

![Potential energy surface and reaction coordinate](image)

Fig 1.1 a) 2-dimensional cross section of a potential surface, having valleys along $XY+Z$ and $X+YZ$ with a barrier at $R(XY) \approx R(YZ)$. The full lines connect points of equal potential energy. b) Potential energy variation following the dotted line (reaction coordinate) of Fig 1.1 a). The straight lines schematically show how the potential barrier may be seen as resulting from an avoided crossing. The ‘zero-order’ crossing potential curves are coupled by $V_{ab}$.

During the reaction, the system changes electronic state, from the $XY$ molecule to the $YZ$ molecule, although both may be of the same symmetry. The barrier can therefore be seen as resulting from an avoided crossing, in going from one state to the other. In molecular ground-states, where most chemistry occur in nature, the potential barrier is often smooth, and the molecule will follow the adiabatic, avoided crossing path. This correspond to a large coupling element of the crossing states, leading to adiabatic dynamics and the molecule will generally follow the dotted path (schematically). With the advent of the femto-second laser technology, the above reaction may be studied in the time domain (reaction time scale $\approx 10^{-11}$ to $10^{-13}$ s), creating a probability wavepacket (see chapter 4.2) at one end of the reaction coordinate, with enough kinetic energy to run across the barrier. The wavepacket motion may then be...
probed at different times along the reaction by the use of a second femto-second laser pulse. It is of particular interest to follow the wavepacket through the transition state, the barrier in this case. The concept of curve-crossing and non-adiabatic dynamics (see chapter 4.1 for my definition of this term) is therefore perhaps superfluous, when considering ground-state chemical reactions. However, for electronic excited state reactions, e.g. light induced reactions such as light-harvesting processes, combustion chemistry etc, the potential surfaces often cross and result in sharper barriers, in which the molecule may make a transition from one adiabatic path to another in the region of the curve-crossing. The strength of the coupling element thus determine the complexity of the dynamics where the limits of high or low strength lead to simple adiabatic dynamics, while the intermediate strength lead to complicated non-adiabatic dynamics. In a curve-crossing of intermediate strength, the molecule may change electronic state, and thus its chemical properties.

We may take one further step down the ladder of complexity, and study wavepacket dynamics in potential curve-crossings of diatomic, gas phase molecules. Beside elucidating the wavepacket dynamics on its own, chemical oriented applications are, for instance, predissociation (bond breaking, see below) and intra-molecular change of electronic state (e.g. transfer from singlet to triplet manifolds). One pioneering work of wavepacket dynamics in a curve-crossing dissociation was on the NaI diatomic gas phase molecule done by Zewail et al 1989 [2]. Real time femto-second pump-probe spectroscopy monitored how part of the wavepacket leaked out and dissociated each time the bond vibrating wavepacket entered the curve-crossing region.

The work presented in this thesis, continue on the theme of wavepacket dynamics in curve-crossing regions, with particular focus on the case of intermediate coupling strength, performed in diatomic gas phase molecules. As a target molecule, Rb$_2$ was chosen. Curve-crossings, intermediate coupling strengths, time scales of larger than 500 fs, high vapour pressure for intense Rb$_2$ beam, etc determined the choice of Rb$_2$. Working with both experiments and theory, the research is progressing iteratively. Experiments are fruitful both as verification of existing theories, and as a source of new results that stimulate new theoretical understandings. Two systems of the Rb$_2$ molecule, containing curve-crossings, have been used as working media, and studied with pump-probe spectroscopy (wavepacket dynamics).

The first is named the A-state system, and contains the first excited electronic states of ungerade symmetry [3]. The curve-crossing is made by two bound states. The curve crossing coupling strength is in this case intermediate, see chapter 4.1.2, and together with a certain timing of wavepacket fragments, the non-adiabatic dynamics is full of interesting effects. As all potential curves relevant for the pump-probe scheme, as well as the curve crossing coupling element, are available from ab-initio calculations [3] (which does not necessary mean that they are good), these experiments and analysis is of a more physical nature, where the physics of the wavepacket itself, in a crossing region, is investigated in detail. In particular, new types of interference effects were found, as the wavepacket splits and rejoin at the crossing. Two types of experiments were done on this system, vibrational wavepacket dynamics (done in the magic angle, see chap. 4.3) and rotational wavepacket dynamics (anisotropy measurements, chap. 4.3). To our knowledge, the only previously reported experiment on curve-crossing dynamics, of intermediate strength
coupling, is a predissociation study of IBr by Stolow et al [5, 6]. In contrast to our experiments on the A-state system of Rb₂, predissociation arise from the crossing of one bound and one unbound state. As reported in their article, wavepacket interference manifest itself by opening or closing the dissociative ‘drain’ channel, and the lost portion of wavepacket is lost indefinitely from the molecular dynamics, as the molecule dissociates. In the frequency-domain, a closed drain channel correspond to narrow energy eigenstates, while open drain correspond to broad energy eigenstates. The open/closed alternative is set by the phase difference between the two rejoining wavepacket fractions, after each has taken a roundtrip to the left from the crossing along different paths, and the strength of interference is influenced by the spatial overlap and the relative wavepacket amplitudes. Broeckhove et al [7] made a theoretical investigation on wavepacket dynamics in a bound-bound crossing of the N₂ b' and c' states with most attention on the weak coupling strength case. Several articles report on experimental and theoretical work on curve-crossing dynamics of weak coupling strength including bound-bound [8, 9] and bound-unbound states [10, 11, 12, 13]. All these articles report on the wavepacket’s interferometric properties of different kinds.

The second system is named the D-state system. Being a higher-lying electronic state, the number of relevant potential curves is larger, the final states are uncertain, and the system is far more complicated to treat theoretically than the A-state system. Based on the continuous-wave laser results reported by Breford and Engelke [14] and the pump-probe results of Zhang et al [15], we performed pump-probe experiments in a molecular beam on the D-state system. A single perturbing state was expected to predissociate the D state. However, our results contained structures that cannot be explained by only two involved crossing states. Analysis of the obtained data resulted in the following proposed scheme: The dynamics essentially proceeded in two independent parts, the laser pump exciting one wavepacket in each of two different electronic states. One goes through curve crossing dynamics with at least two perturbing states, one bound and one unbound. The other make bound oscillations in a single state. These oscillations are quite unusual, though, due to a `shelf shape’ of the potential curve [3]. The shelf also originates from a set of avoided crossings of states of identical symmetries, but the electronic coupling strength is so strong that it leads to highly adiabatic dynamics, similar to the above XYZ molecule reaction example. We also propose final potential shapes and coupling element strengths, as a result of the numerical simulations.

Chronologically, the D-state system was studied before the A-state system, and at that time, a simpler numerical simulation program was available, which has been developed further for the A state analysis. Continuing analysis of the D state system is awaiting.

Experimentally, the use of two independent optical parametric amplifiers (Topas), one for the laser pump beam and one for the laser probe beam, enable us to pick the two wavelengths independently from a continuous range of 250 – 2500 nm. A decrease of pump wavelength excites a wavepacket with higher energy, and a change of probe wavelength changes the probe position (in the inter-nuclear distance). For the work included in this thesis, only the pump wavelength has been scanned in the neighbourhood above a curve-crossing, to study the dynamics dependence on the wavepacket energy. Experiments on the D-state system with scanning probe
wavelength is waiting to be analysed. The design of the optical collection of fluorescence from the laser-molecule interaction point in the near-effusive beam, was optimised for signal strength. This provides us with good signal to noise level, keeping the laser intensity low (not to induce non-linear effects. With increased signal to noise level, finer details of the signals can be studied and provide more information. This was critical for the anisotropy measurements (chapter 5.3) on the A state system, where small oscillations are resolved, in which the curve-crossing effects are hidden. In comparison to ion collection techniques, fluorescence detection has much lower sensitivity [18].

In principal, any experiment on any molecular curve-crossing is unique, with different experimental conditions and different molecular parameters, such as potential curve shapes and coupling strengths. In this sense, any successful match between experiment and theory is fruitful, at least for verification purpose, which set current understandings on a more solid ground.

For the work on the A-state system, a few noteworthy new angles on curve-crossing dynamics study was met. First, the shape of the two crossing curves in combination with intermediate coupling strength has outstanding properties. The two states are both bound, making each fragment of the splitted wavepacket return to the crossing. The timing of the left hand side (with respect to the crossing point) is perfect for interference effects of returning wavepackets to the crossing. Secondly, thermal effects on these interferences were studied, having, experimentally, hot molecules ($\approx 700$ K) in the beam. The fingerprint of the interference and scanning possibilities (by changing pump laser wavelength) are shown to survive thermal averaging. Thirdly, rotational wavepacket study, via anisotropy measurements, give complementary signs of the curve-crossing dynamics, as both rotational and vibrational dynamics occur in general simultaneously (if not measured at ‘magic angle’, where rotation only contribute a centrifugal correction term to the potential curves for the pure vibrational dynamics). As mentioned above, good signal to noise level is required to resolve these signs, since the anisotropy is calculated from a small difference of large signal levels. Experimental measuring time was up to 30 hours. The analysis of our anisotropy measurements follow the outline by Zewail et. al. [41], with the exception that in our case, the vibration dynamics do not cancel out in the thermal averaging. This fact we propose is the origin of the small oscillating structure, superimposed on the anisotropy time trace.

On the analysis side, we have continuously increased the complexity of the numerical simulation programs, using the Fourier transform split operator technique [16]. The construction of our program relies on taking short enough time steps, where the result converge to the ‘true’ result (solution of the time dependent Schrödinger equation) as the time step-size approach zero. This allows us to use any number of potential curves, with free choice of coupling elements of any size and any number. The couplings may be time-independent intra-molecular or time-dependent electro-magnetically induced, and may be varying with inter-nuclear distance. The trick is to approximately treat the full system as a set of pair-wise coupled states, where the approximation is less bad the smaller the step size is. It can be shown [17] that analytical solution only exists up to three coupled potential curves. And since the minimum of states involved are four in a pump-probe scheme containing at least two
crossing intermediate states, the advantage is obvious. Further, thermal averaging, although time consuming, enable us to make direct comparison with experiment at T= 700 K.

The organisation of the thesis is the following: After a short presentation of the molecular systems and model systems an experimental setup survey follows. Two different Rb$_2$ beam sources have been used, of which only the second one was employed for the experiments in the attached papers of this thesis. The first source, a crossed molecular beam setup, was designed to cool the molecules, and results of its characterising work is presented. However, the density and stability of the Rb$_2$ molecules at the laser-molecule interaction point proved to be too poor for pump-probe experiments. The experience from its performance was used in the design of the second source, which overcame the problems of the first source.

In the beginning of the theoretical chapter, the potential energy curves, with crossings and coupling elements, are introduced and shortly defined. For the introduction of the vibrational wavepacket, a model system consisting of harmonic potentials is employed for easier recognition of well-known results. Still, it is approximating the real Rb$_2$ A-state system potential curves, making the jump to the real molecule small. It will also be used, in chapter 5.1, to investigate change of wavepacket behaviour when artificially manipulating the shape of the potential curves. The treatment start with analytical derivation of the wavepacket. Auto-correlation numerical calculations (using the simulation program), reveal the wavepacket’s structure. A taste of the curve-crossing dynamics is given by turning on the coupling element of the two crossed harmonic potential curves. For the introduction of the rotational wavepacket, simple semi-classical modelling and classical arguments introduce the ideas, and we will thereafter see that it fully agrees with a quantum mechanical calculation in the limit of large rotation (J > 5). The simple anisotropy model is then used as a part of an approximate analysis of the real Rb$_2$ A-state system anisotropy.

Chapter five then summarize the vibrational non-adiabatic wavepacket dynamics work on the A-and D-systems of Rb$_2$ presented in papers 1-3, followed by the anisotropy work on the A-state system of Rb$_2$ presented in paper 4. Lastly, in chapter six, I glimpse into the near future of possible continuing research on curve-crossing quantum wavepacket dynamics.
2 Molecular systems

2.1 A-and D-state systems of Rb$_2$

The study in this thesis concerns the quantum wavepacket dynamics in two systems of the Rb$_2$ molecule in a collision-free gas phase environment. The first system will be named ‘the A-state system’ and the second ‘the D-state system’. To set the stage, Fig 2.1 shows the dominant potential curves [3], laser pump and probe transitions and detection fluorescence transitions, (see the following chapters for details). For the vibration dynamics, a rotation centrifugal term ( see chapter 4.2.2 a)) is added to the potential curves of Fig 2.1.

![Fig 2.1 a) A-state system. Schematic wave packets are shown in the ground-intermediate-and final states. Detection fluorescence is the atomic 5P$_{3/2}$ → 5S$_{1/2}$ transition. The inset illustrate the avoided crossing picture, when S-O interaction is taken in account. b) D-state system. The ground state, X $^1$Σ$_g^+$ is omitted in the figure. The probe has two simultaneous, but independent probe positions. Detection is the atomic 8P → 5S.](image)

The A-state system, consisting of the first excited singlet electronic state $A$ $^1$Σ$_u^+$ and the lowest triplet state $b$ $^3$Π$_u$, is well suited for general wavepacket study. The phenomena of vibrational wavepacket interference is the main issue, which take place at the crossing of the two intermediate coupled electronic states. In addition to vibrational wave packet dynamics, rotational dynamics was studied on this system as well. The question here to answer is how the crossing of the intermediate states influences an anisotropy measurement.

The D-state system is more complex, due to the larger number of coupled states [3]. Further, the structure of the final, probe-excited, states are not known. The analysis shows that two electronic states are excited simultaneously by the pump, and that their following dynamics is independent of each other. One performs adiabatic oscillations in a so called ‘shelf state’. The other make transitions to coupled states, however, of less coupling strength than the case of the A-state system.
2.2 Model systems

As a means of introducing the general vibrational wavepacket dynamics theoretically, a simplified model of the A-state system will be used as a benchmark. The \( A^1\Sigma_u \) state is here approximated by a harmonic potential of similar shape, and same goes for the coupled \( b^3\Pi_u \) state. By doing this, we can easily recognise results which are familiar for the harmonic oscillator, and still have a connection to the Rb\(_2\) A-state system. Analytical derivations, classical arguments and numerical simulations go hand in hand, due to the complexity of the wavepacket concept. The coupling element between the harmonic \( A^1\Sigma_u \) and \( b^3\Pi_u \) substitute state can freely be turned off and on in the simulations.

Introducing the concepts needed for a study of molecular rotation, a simple \( \Sigma-\Sigma-\Sigma \) state model is used, where ground state, intermediate state, and final state are all of \( \Sigma \) symmetry. The detection will be assumed isotropic. This model system will also be used as a part of the analysis of the anisotropy measurement on the A-state system.
3 Experimental

The ‘gas phase’ setup in the fs lab is sketched in Fig 3.1.

![Fig 3.1 Rb₂ pump-probe experimental setup.](image)

3.1 Optics

The Ti: Sapphire amplified mode locked fiber femtosecond laser synchronously pumps two independent optical parametric amplifiers, by the use of a beam splitter for the fs-laser output beam. In combination with frequency mixing, output wavelength range is 250 to 2500 nm. Not shown in the figure are the prism compressors, which consists of two prisms each. The prisms also act as wavelength separator, since the Topas output beam consists of many sum or difference frequencies.

CPA 2001 Femtosecond laser characteristics:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power</td>
<td>850 mW average</td>
</tr>
<tr>
<td>Repetition freq.</td>
<td>1000 Hz</td>
</tr>
<tr>
<td>Wavelength, fundamental</td>
<td>775 nm</td>
</tr>
<tr>
<td>Pulse length, FWHM</td>
<td>120 fs</td>
</tr>
</tbody>
</table>

Topas:

- Example: 430 nm, 5 mW average, Pulse length ≈ 120 fs, Δλ = 2.7 nm
- 927 nm, 2 mW average, Pulse length ≈ 120 fs, Δλ = 11.5 nm

A Glan-laser polarizing prism has been used to analyse the laser beam polarisation quality before entering the experimental zone. The Glan prism has a very high extinction ratio over the wavelength range 350-2300 nm, enabling us to assure high purity of the linear polarisation (neglectable ellipticity), and polarisation angle to within +/-1 degree. The light beams emerging from the prism compressor, are highly linearly polarised in a horizontal plane.
A Berek compensator was used to turn the polarisation angle of one of the beams. It consist of a uniaxial nonlinear crystal which is tilted to a proper angle in order to act as a λ/2 waveplate for the particular beam wavelength ( tilting changes the effective extraordinary refracting index ). Continuous polarisation rotation can thus be achieved, where the rotated angle is twice the angle between the input laser polarisation and the waveplate’s fast axis. Careful analysis of the rotated beam was performed with the Glan polarizing prism, to ensure high linear polarisation purity.

The optical setup for fluorescence capture is designed for good detection signal strength. The detection lens of $\phi = 50$ mm and focal length $f = 50$ mm, captures about 1/6 of the $4\pi$ solid angle.

The fluorescence is spectrally filtered before it’s recorded on the photo multiplier (PM) tube. Filtering is achieved either by colour filter, interference filter, or Yvon-Jobin monochromator ( $\approx 1$ nm bandwidth ) together with the spectral response curve of the PM tube.

3.2 Characterisation of pump and probe pulses

The spectral distribution of the pump and probe pulses are measured in a Chromex grating spectrograph having spectral range 200 – 1100 nm. Fig 3.2 show one such spectrum.

![Spectral distribution of the pump pulse, here 424.5 nm, for the D-state system experiments. The full curve is a gaussian fit. FWHM = 2.4 nm.](image)

The temporal distribution of the frequencies of the pulse, the chirp, has not been measured directly. If the timescale for the dynamics in the molecule is sufficiently much larger than the temporal pulse width, about 120 fs, the chirp should play a minor role. In our case, dynamic timescales of down to a few hundred fs occur, thus an interferometric autocorrelation measurement of the chirp would eliminate the uncertainty of possible chirp effects. However, from the measured frequency bandwidth and temporal width from any of the techniques described below, we can estimate how far from transform limited (chirp-free) the pulses are.
Taking the 927 nm laser pulse as an example:

\[ \lambda_0 = 927 \text{ nm} \]
\[ \Delta \lambda = 11.5 \text{ nm} \]
\[ \Delta t = 120 \text{ fs} \]

\[ \rightarrow |\Delta t \Delta \nu| = \frac{c}{\lambda_0^2} \Delta t \Delta \lambda = 0.48 \] (3.1)

which is only slightly larger than the value 0.44 for transform limited gaussian pulses. Hence we expect the chirp to be small and not significant for our experiments.

If a reflex of the laser pulse is detected by a photodiode and sent to an oscilloscope, the pulse seen is a few ns wide due to the ‘slow’ response time of the electronics. The time profile of the laser pulse has to be measured in a somewhat indirect way, since no electronics has fast enough response time. Crosscorrelation or autocorrelation measurements were done.

Crosscorrelation:
This is the time profile of the combined pump and probe pulses. That is, both pump and probe beams are overlapped in a medium having a nonlinear response, in our case a two-photon absorption process (and 3 photons for the A-state experiments).

a) In a photodiode
The diode is sensitive for the sum frequency of the pump and probe pulse, therefore an electric pulse is produced when pump and probe overlap, both in space and in time. The better the overlap, the larger amplitude of the electric pulse (non-saturated diode). Scanning the probe pulse, by moving the delay mirror, the overlap time profile is recorded. The time resolution of the delay stage is 3.3 fs, corresponding to a mirror position shift of 0.5 micrometer.

b) In acetone gas, (for the D-state system experiments)
Instead of using a photodiode outside the vacuum chamber, the chamber is filled with acetone gas and crosscorrelation is made in situ. The acetone molecule’s first excited state fits energetically with the sum of one pump and one probe photon, Fig 3.3. The two-photon absorption is monitored by the subsequent fluorescence when the excited acetone molecule decay back to the ground state. Since the laser beam geometries are exactly the same as in the Rb\(_2\) experiment, this crosscorrelation technique was used as ‘time zero’ calibration of the Rb\(_2\) experiments. We simply exchange the Rb\(_2\) molecule with the acetone molecule.
Fig 3.3 Crosscorrelation in acetone gas. Pump = 429nm, probe = 927nm. The full curve is a gaussian fit. FWHM = 180 fs. Only when pump and probe pulse overlap in time and position, can one pump and one probe photon together excite the acetone molecule.

The two-photon absorption is proportional to the second order correlation function [18]:

\[ S \propto \langle I_1(t) I_2(t + \tau) \rangle \]  \hspace{1cm} (3.2)

If both pulses are assumed to be gaussian, this function is a gaussian, too, with maximum at \( \tau = 0 \), and a halfwidth of \( \sqrt{2} \) times each pulse’s halfwidth. The measured cross-correlation intensity-halfwidth is 180 fs.

Recalling that a distance of 10 µm equals 30 fs for the light, accuracy of time zero within 50 fs can only be achieved in situ, where the Rb\(_2\) molecules are excited. All experimental time traces in paper 1 are time-calibrated with acetone gas. Repeating the acetone calibration, the error of the calibration is estimated to be less than 50 fs.

c) In Rb atoms (for the A-state system experiments)  
Time-zero calibration is made in situ, by nonresonant excitation of atomic Rb \( ^2P \rightarrow ^2S \) fluorescence, as \( 2 \cdot \lambda_{\text{pump}} + 1 \cdot \lambda_{\text{probe}} \) match the transition.

Autocorrelation:  
An instrument, similar to a Michelson interferometer, is used to measure autocorrelation of one laser beam. The idea is to measure the time profile of the femtosecond pulse by splitting it up into two fractions, and then to scan (in time) one of them across the other in a nonlinear medium, at a small angle. Second harmonic generation is produced when the two pulses overlap in time and space. Conserving the momentum, the resultant second harmonic beam will propagate inbetween the two fundamental pulses, giving a background-free signal in the detection photodiode. The photodiode signal is fed to a boxcar integrator, which is connected to the AD card in the computer.
3.3 Electronics and software

The electronic setup, as used for the Rb$_2$ pump probe experiments, is illustrated in Fig 3.4. A trigger signal from the laser pulse controls the timing of the system.

![Fig 3.4 The electronic-and optical detection setup as used in the Rb$_2$ pump-probe experiments.](image)

The heart of the electronics is the SR 400 photon counter, counting electronic photon signals from the PM tube, averaging the signals of 1000 laser-shots (during 1 second; laser shot frequency = 1000 Hz), and feeding the result into the software. Averaging is essential, since even the average of the signal level of 1000 shots fluctuate around 20% of the signal level. The counter is gated, collecting photon signals within a time window after the laser shot. This suppress background noise greatly, as the molecular fluorescence is lasting much shorter than the time in-between laser shots.

![Fig 3.5 Software layout.](image)
The lab-computer talks and listens to the instruments via a GPIB card and an AD/DA Card, Fig 3.5. The GPIB communication is in general faster than serial communication. These two cards are not directly compatible with the used Labview software. Therefore, a DLL library with C code subroutines was written as a mid-step to communicate with the instruments. A DLL file (Dynamic Link Library) needs only be compiled once, and can then be used from non-C code programs. Writing in C code has the advantage of being at least ten times faster then Labview code. In our present setup, the averaging of fluorescence, from 1000 pulses at 1000 Hz repetition frequency, is done in the SR 400 photon counter directly, putting less requirement on computer speed.

The Labview software is a high-level graphical language, designed to communicate with lab instruments. Programming is done purely graphically, with symbols and execution lines. Via Call library functions, the program communicate with the instruments. Basically the program scans the delay mirror, and collects the SR 400 photon counts.

3.4 Molecular beam machine

In a molecular beam, effusive or supersonic, there is a collision free environment, simplifying the analysis greatly. Even in a femtosecond pump-probe experiment, the fluorescence detected has a time span of, say, 1 µs, giving plenty of time for collision population transfer. The molecular density between the laser-molecule interaction point and the fluorescence capture lens is low, minimising self absorption. Using a supersonic design, cooling of the molecule is achieved [18]. Also in an near-effusive molecular beam, a slight cooling in the oven hole is present, where collisions in the hole transfer heat energy into kinetic energy. Rotationally and vibrationally cool molecules simplify the analysis of the experiment by having less states populated in the ground state, giving less energy spread of the excited wave packets.

The molecular beam assembly is mounted inside a vacuum chamber pumped by a diffusion pump. The near-effusive beam has a negligible gas load on the overall chamber pressure, while the pulsed supersonic beam has an appreciable gas load. Vacuum pressure is below $5 \times 10^{-6}$ mbar, using only the near-effusive beam, and around $10^{-4}$ mbar using both near-effusive and supersonic beams. The mean free path [19] at $5 \times 10^{-6}$ mbar is about 5 m. At an oven-temperature of 700 K, the Rb$_2$ density is $10^{14}$ molecules / mm$^3$ inside the oven, giving a mean free path of about 5 µm, indicating that we do have some collisions within the 50 µm oven-hole.

Preceding our current molecular beam assembly, the 2$^{nd}$ source, I tested and characterised a crossing beam assembly, the 1$^{st}$ source. It was intended to be used in our femto second experiments, but proved to be unsuccessful in the required stability and density of the Rb$_2$ beam at the laser-molecule interaction point, 50 mm downstream the Rb$_2$ oven nozzle. As the experience from this work was used in the design of the 2$^{nd}$ source, I will present the outcome of the tests of the 1$^{st}$ source here, while the results obtained in the 2$^{nd}$ source are given in later chapters and in the attached papers. The tests on the 1$^{st}$ source investigated a) the stability and density of the beam b) the collision free environment in the beam c) the kicked-down Rb$_2$ molecule-pulses by the crossed pulsed supersonic Ar beam and d) the cooling of the kicked-down Rb$_2$ molecules.
3.4.1 First Rb$_2$ source

Crossed molecular beams:

Fig 3.6 Crossed beam design. The Rb$_2$ molecules are kicked down by supersonic Ar atom pulses, and detected by LIF.

Solid Rb metal is put into the near-effusive oven source, heated by wires covering the oven, Fig 3.6. A thermocouple is monitoring temperature, which ranges from 200 to 450 °C. At 450 °C, the beam consist of roughly 1 % Rb$_2$ and 99 % Rb atoms [20]. This beam is crossed by a pulsed supersonic Ar atom beam. In the collisions between Rb$_2$ and Ar atoms, heat is transferred from the hot Rb$_2$ molecules to the cold Ar atoms. The pulsed operation of the supersonic nozzle is there to reduce the gas load on the diffusion pump. The kicked-down Rb$_2$ molecules are detected by laser induced fluorescence, LIF. The molecular beam assembly can be moved in all directions, enabling different laser-molecule interaction points.

Fig 3.7 Fluorescence spectrum of Rb$_2$ C state

Using an H20 Jobin Yvon monochromator and a plotter, fig 3.7 shows the LIF spectrum of the Rb$_2$ C state excited by the 476 nm Ar ion laser line is shown. Also,
a few potential curves [3] are shown. Only the Rb$_2$ beam is used, and is lowered in order to overlap the laser beam. Note the intense 780 nm fluorescence, and the total absence of 794 nm fluorescence. This demonstrates an experimental 'proof' of a collision free environment in the beam. The C state is strongly predissociated by the (2)$^3\Sigma_u^+$ state, which correlates to the upper 5P atomic state, the 5P$_{3/2}$, including the spin-orbit interaction. The recipe for adiabatic spin-orbit correlation limits is given in the appendix. Collisions transfer population to the 5P$_{1/2}$ atomic state, as seen by J.M. Brom Jr. et al. [20], who performed this experiment in a heat pipe oven. The peak at 610 nm is proposed to be fluorescence from (2)$^3\Sigma_u^+$ to very high-lying vibrational levels (and continuum) of the X $^1\Sigma_g^+$ ground state. The (2)$^1\Sigma_u^+$ state crosses the C $^1\Pi_u^+$ state and they couple via the ‘L-uncoupling matrix element’ [24]. Further, cascading B $\rightarrow$ X transition gives signal around 650 nm.

Fig 3.8 Time trace of a kicked-down Rb$_2$ pulse, excited by Ar ion 476 nm and detected atomic fluorescence at 780 nm, using a 780 nm interference filter.

Figure 3.8 shows a typical kicked-down Rb$_2$ pulse. The continuous Rb$_2$ effusive beam is crossed by the pulsed Ar atom supersonic beam, and the kicked down Rb$_2$ molecules are detected by LIF. The supersonic nozzle valve has a pulse width of about 1.5 ms and repetition frequency of maximum 100 Hz.

Most effort was put on proving the cooling mechanism, which, looking at Fig 3.9, could not be confirmed. A few scans pointed toward a cooling effect, but the instability of the signal made it hard to reproduce the cooled spectrums. Apart from the oven instability (which was greatly improved in the second source), mode jumping of the dye laser added extra instability. The tactics to show the cooling of the Rb$_2$ molecules was the following: The X $\rightarrow$ B (one of few unperturbed states) absorption spectrum was recorded using Ar ion laser pumped dye laser, see Fig 3.9. DCM was used as lasing media and scanning range was 650 to 680 nm. A long-pass colour filter at 695 nm was used as detection filter, to spectrally separate out fluorescence from the laser light. The beam assembly was repetitively moved up and down (up with Ar beam on, down with Ar beam off), in order to compare non-kicked to kicked Rb$_2$ molecules. If cooling is
present, electronic ground state, $X^1\Sigma_g^+$, population in higher vibrational levels is suppressed, and peaks in the spectra originating from higher ground state levels should decrease in intensity, compared to the $v'' = 0$ peaks.

![Absorption spectrum](image)

**Fig 3.9** Absorption spectrum of the $X^1\Sigma_g^+ \rightarrow B^1\Pi_u^-$ transition, of the kicked down Rb$_2$ molecules by the supersonic Ar atom beam. The numbers show the vibrational progressions, $v''-v'$, and the wavelength axis is calibrated against ref. [21], and an H20 Jobin Yvon monochromator.

**Drawbacks of the apparatus:**

- **Stability of the Rb$_2$ near-effusive beam.** The 50 µm oven hole has a tendency to clog up. Since there is no separate heating for the hole, one cannot keep the hole at a higher temperature then the rest of the oven to prevent condensing in the hole.

- **Density of the Rb$_2$ near-effusive beam.** The beam density distribution is approximately proportional to $\cos \theta$, where $\theta$ is the angle from the centre direction [22]. Thus, only a small portion of the total flux, in the centre direction, can be utilized. Furthermore, the beam density decreases with the square of the distance from the hole. In this design, the distance from the oven hole to laser interaction point is around 50 mm. Also, the argon beam will only kick down a portion of the effusive Rb$_2$ beam, but this loss should be compensated to some extent by the cooling of the Rb$_2$, putting more molecules in the ground state, from where they are excited. Another limitation is the maximum supersonic nozzle frequency of 100 Hz, thus it could only utilize one tenth of the fs laser pulses.

**3.4.2 Second Rb$_2$ source**

**one effusive beam:**

A second, single beam, Rb$_2$ source was designed and built, Fig 3.10. Higher molecule density, more stable beam, and the ability to change atom / molecule ratio was the goal which was also achieved.
Fig 3.10 Single effusive beam oven design. T1 and T2 are two independent heating thermo-coax cables. Upper and lower temperatures are monitored by two thermo-couples.

The oven is situated inside a cooled copper house with a conical front, shaped to maximize fluorescence capture angle. The distance from oven nose, the nozzle, to laser-molecule interaction point is now only 3-4 mm. Two, independently operated, thermo coax cables heat the front and bottom, making it possible to keep the front at a higher temperature than the bottom, to prevent Rb condensing in the hole. The possibility of changing the front temperature, T2, while keeping the bottom temperature, T1, constant also permits a change of atomic/molecular ratio in the beam. A constant T1 gives a constant vapour pressure. Then, by increasing T2, the increased heat at the front will dissociate molecules into atoms, thereby decreasing molecular content. This tool was used often to investigate if the measured signal is only due to excited molecules or due to excited atoms. Running temperatures for Rb\textsubscript{2} has been around 750 K at the front and 700 K at the bottom.

This oven has been used in all our beam experiments done with the femtosecond laser, which are presented in the rest of the thesis.

### 3.5 A-and D-state experiment specific details

**A-state system:**

- **Pump:** 865-942 nm, 2 µJ per pulse, 1kHz
- **Probe:** 1700 nm, 2 µJ per pulse, 1kHz

Probe beam constant vertical polarisation at the laser-molecule interaction point. Pump beam set to nominal magic angle 54.7 ° with respect to the probe polarisation for the vibrational wavepacket experiment. Pump beam set to alternatively vertical and horizontal polarisation for the anisotropy experiment.

The oven temperature was held at 700 K with slightly hotter nozzle.
Since time zero calibration is obtained in a non-resonant Rb atomic transition, the only change done to record the cross-correlation was to raise the front temperature of the oven to create a beam of mostly Rb atoms. For the cross-correlation fluorescence detection (at 360 nm), the coloured glass filter UG 11 was used in combination with the photo multiplier, PM, tube 1P28. The filter transmits at 250-400 nm and somewhat at 700-750 nm. The PM tube is sensitive at 185-650 nm.

Detection of fluorescence at 780 nm was done via an interference filter at 780 nm in combination with the PM tube R928. The filter has a bandwidth of 10 nm and was mounted in the parallel part of the optical fluorescence collection, to avoid transmission abnormalities. The PM tube is sensitive at 185-900 nm.

For checking of absence of 794 nm fluorescence (can only result from unwanted multi photon excitation), an interference filter at 794 +/-5nm was used.

The rather short lifetime of the 5p atomic states of around 30 ns [23], sets the photon counter gate width of 100 ns, starting immediately after the laser pulse (photon counter triggered by a photodiode detecting a reflex of the laser pulses).

D-state system:

Pump: 425-432 nm, 5 µJ per pulse, 1kHz
Probe: 927nm, 2 µJ per pulse, 1kHz

Probe beam constant vertical polarisation at the laser-molecule interaction point. Pump beam set to nominal magic angle 54.7° with respect to the probe polarisation for the vibrational wavepacket experiment.

For time zero calibration, the vaccum chamber was prior to the Rb2 experiment filled with acetone gas. The cross correlation was obtained, and acetone pumped out before heating up the oven.

The oven temperature was held at 700 K with slightly hotter nozzle.

Fluorescence detection (at around 350 nm) was obtained by the use of the UG 11 in combination with the PM tube 1P28. As the lifetime of these high lying atomic states are rather large, a few hundred ns, the photon counter gate was set to 800 ns, starting immediately after the laser pulse.
4 Theoretical

The theory given here is meant to be the necessary background needed for the specific experiments and analysis presented in this thesis. For example, the vibrational wavepacket theory is for simplicity put on a wavefunction basis, while the rotational anisotropy analysis is better handled using the density matrix.

4.1 Definition of Rb\textsubscript{2} molecular potential curves

The theory is based on the belief that there exist ‘true’ energy eigenvalues with corresponding eigenstates of the ‘true’ (T) time-independent Schrödinger equation [24]:

\[ H^T \Psi^T = E^T \Psi^T \]  

(4.1)

A comment often used on eq 4.1 is that it is much easier to write than to solve. It is of infinite space, and as such, we can immediately give up the hope of finding a ‘true’ solution. Even an experimental effort in achieving the solution, is hopeless, since, for instance, the very act of studying the molecule affects the molecule itself. Nevertheless, we may find approximate solutions, both theoretically and experimentally, and the degree of effort determines the ‘quality’ of these, for instance the solutions of the energy eigenvalues. Experimentally, the laser beam intensity is kept to a minimum, to minimize the disturbance on the molecular structure, and the ‘true’ energy eigenvalues may be defined to be the result of high-resolution spectroscopy. However, as we shall see in the chapter 4.2.2 c), the accuracy of the energy levels depend on the time scale of the measurement. Theoretically, approximations to eq (1) are necessary, and connected to these, potential curves may be defined and calculated (fig 1), on which the wavepackets will reside. The central part is the Born-Oppenheimer approximation. In this short review, only certain important variable-or parameter-dependencies will be stated. To start with, the relativistic spin-orbit Hamiltonian is completely ignored.

4.1.1 B-O approximation

The origin of this approximation is that the nuclei’s are much heavier than the electrons, by a factor of $1.5 \cdot 10^5$ for the rubidium atom. For each inter-nuclear separation, the light electrons have time to adjust their motions accordingly. This means that the electronic and nuclear structure and motions may be treated separately, they decouple. The outcome of this basic assumption is [24],

- The wavefunction may be written as a product of electronic, $\phi$ and nuclear parts $\chi$ (vibration, rotation)

\[ \Psi = \phi(R) \chi(R) \]  

(4.2)

- The Hamiltonian is separated in $H = T^N + T^e + V$ which leads to energy levels of the form $E = E^{el} + G(v) + F(J)$. The Hamiltonian describes in order; nuclear kinetic, electron kinetic and electrostatic potential energy operators.

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• Potential curves may be defined, in which the nuclei move as vibration motion. If rotation and vibration decouple as well, \( \chi = \chi_{\text{vib}} \chi_{\text{rot}} \), the rotation energy is added to the potential curve as a term \( \propto J(J+1)/R^2 \).

Depending on which terms to neglect in the Hamiltonian \( H \), different potential curves are obtained with corresponding vibrational and rotational energy levels. Among these are the so called adiabatic and diabatic potential curves. Note that both of these can be written in the same form as eq (2), where electronic and nuclear motion are separated. As this is an approximation per definition, the potential curves must be seen as an approximate mathematical construction, and to obtain the ‘true’ solution, couplings between potential curves are necessary. Most of the time, the above outlined B-O approximation gives satisfactory approximate solution (no couplings among the states), but in neighbourhoods of curve crossings, the B-O fail locally, eq (2) is bad, and coupling terms have to be inserted. The B-O solutions, can however, always be used as a basis, in which to expand the ‘true’ eigenfunctions.

Many options in the approximate approach to solving eq (1) are possible. Different terms in the Hamiltonian may be completely neglected, and among the included terms, different separations in a zero order, \( H_0 \) and a perturbation, \( H' \) are possible. In the following, I will briefly outline the methods used in this thesis.

Starting with the potential curves, we utilised the ab initio calculated potential curves by Park et al [3]. Without knowing the detailed calculations, the general procedure is the following: First, exclude the spin-orbit Hamiltonian. Doing this, the potentials obtained are Born-Oppenheimer type potentials, where the electronic structure is calculated for every fixed \( R \). This step, the field of quantum chemistry, also depends on approximations and different zero order Hamiltonians. For example, choice of Hund’s case, C-I techniques, molecular orbital configurations, electron-electron static interaction etc. These may depend on \( R \), e.g. Hund’s case a) is appropriate at small \( R \), while Hund’s case c) is better at large \( R \), where potential curves come close. By optimising this electronic part, \( H_0^{\text{el}} \), adiabatic potential curves are obtained, where potential curves of the same symmetry do not cross. These states may couple via the non-adiabatic term, \( H_0^{\text{el}} \), adiabatic potential curves are obtained, where potential curves of the same symmetry do not cross. These states may couple via the non-adiabatic term, which are differentials of the electronic wavefunction with respect to \( R \). These we assume are small, and trust that the adiabatic approach by Park is appropriate. In the strict definition [24], of an adiabatic potential, the diagonal \( R \)-derivatives on the electronic wavefunction are included. However, this correction should be small, and within uncertainties of the absolute energy of potential curves, in comparing different theoretical works [25, 3], it is not of high importance to us. The ‘shelf state’ is a typical example of an adiabatic state originating from several avoided crossings. States of different symmetry, may still cross because they don’t feel each other under the assumptions taken above.

### 4.1.2 Spin-orbit coupling

Next, we include the spin-orbit Hamiltonian, \( H^{\text{SO}} \) (off diagonal terms most important for us). This interaction is expected to be the dominant among the neglected terms of the full Hamiltonian. It increases with atomic weight, is a one electron interaction and may couple states of different symmetries (still \( \Delta \Omega = 0 \)).
Introducing this extra part of the Hamiltonian, things are turned upside down, when it comes to the labelling adiabatic/diabatic. The potential curves of Park et al [3], which were called adiabatic, without consideration of $H^{SO}$, are now called diabatic (with respect to $H^{SO}$). Possible R-derivatives on electronic wavefunctions, as mentioned above, are neglected. The A and b states is an example of crossing diabatic potential curves, coupled by off-diagonal, R-dependent matrix element $V_{SO}$ of the potential part of the Hamiltonian. In other words, our definition of diabatic states, is a representation when two interacting potential curves cross, when the perturbation, $V_{SO}$, is removed. This is the approach used in our numerical simulations. For interpretations, we sometimes transform the diabatic potential states to adiabatic (with respect to $H^{SO}$). The potential part of the Hamiltonian is then diagonalised, and we obtain non-crossing, or avoided crossing, potential curves. Now the coupling appears as off-diagonal, non-adiabatic, terms in the kinetic part of H instead. Which approach is the better, depends on the sizes of off-diagonal terms in either case (and which ones are easier obtained). If the diabatic coupling, $V_{SO}$, is small, the diabatic approach is the better (large non-adiabatic off-diagonal elements). If $V_{SO}$ is large, adiabatic approach is the better (small non-adiabatic, large diabatic off-diagonal elements). In the specific cases of $Rb_2$ studied here, the D state system has relatively small $V_{SO}$ element, and the A state system is in the ‘intermediate’ case. In both cases, the diabatic representation (with respect to $H^{SO}$) was utilised in the numerical simulations, coupled by $V_{SO}$. For a case of larger diabatic $V_{SO}$ term, the numerical simulation program, based on the diabatic representation, may still be used, but smaller time steps would be necessary to obtain the same accuracy.

As a start, we get a very rough, ‘order of magnitude’, estimate of the strength of the spin-orbit coupling by looking at the separated atoms of the $Rb_2$ molecule. The dissociation process is dominated by leaving one atom in the ground state, 5S, (no spin orbit coupling) and one atom in a single electron excited state (or ground state). Being an alkali atom, Rb has a single electron outside closed shells. To first approximation, this excited electron provides the atom’s spin and angular momentum, and the other electrons screen the nuclei, depending on which orbital the excited electron is in. The total angular momentum can take two values for an electron of spin $\frac{1}{2}$, namely $j = 1 + s$ or $j = 1 - s$. The atomic levels are doublets and split into two by the spin orbit fine-structure.

The size of the S-O interaction for a one electron system of nuclear charge, $Z$, is [26]

$$V_{SO} \propto \frac{Z^4}{n^3 l(l+1/2)(l+1)}$$

(4.3)

where $H_{SO} \propto V_{SO} (l \cdot s)$

$n$ is the main quantum number and $l$ is the angular momentum of the electron

This formula does not account for the other electrons (e.g. screening) and is only indicative. $V_{SO}$ increases with nuclear charge meaning that heavier atoms have in general larger spin-orbit coupling. Having nuclear charge $Z=37$, Rb does have a considerable S-O strength.
Moreover, $\nu_{SO}$ decreases with the main quantum number, $n$. This leads to a lower S-O coupling strength for the Rb$_2$ D state system ($\approx 20 \text{ cm}^{-1}$) than for the A state system ($\approx 70 \text{ cm}^{-1}$). The experimental values of the S-O energy split of the 5P atomic state is 238 cm$^{-1}$ (to which the A state, and b state correlate) and 78 cm$^{-1}$ for 6P (to which the D state correlate) [27].

A state system:
At large $R > 20 \text{ Å}$, one can estimate the S-O couplings for the A and b states ($\Omega = 0^+$) from the atomic energy separation, 238 cm$^{-1}$. The outcome is that the b state is shifted down by 79 cm$^{-1}$ and the coupling element is 111.7 cm$^{-1}$ [25]. The shift is within the absolute energy uncertainty of the potential curves, so we keep this value as $R$ is decreased. The S-O coupling element first decreases as the atoms are brought together and the electronic clouds start to overlap. Then it increases again as the nuclei come close, as $Z_{\text{eff}}$ increase for the more atomic-like molecule. An ab initio calculated S-O coupling element as a function of $R$ [4] was rescaled to the correct dissociation limit, and used in the analysis, having a value near 70 cm$^{-1}$ at the crossing between the A and b state at $R \approx 9 \text{ a.u}$. This is comparable with an upper limit, pure precession, estimate [24] of 79 cm$^{-1}$.

D state system:
A similar, pure precession, estimate of S-O coupling strengths of states dissociating to 6P (e.g. the D state) gives a value between 18 and 26 cm$^{-1}$[24], depending on which states are involved. These values are only indicative, as the state coupling to $D^1\Pi_u$ ($(4)^3\Sigma^+_u$, $(1)^3\Delta_u$) have another dissociation limits, and the multitude of other states around the D state at the wave packet region, mixes the electronic orbital configurations. Thus, a value of 20 cm$^{-1}$ was chosen for both $D^1\Pi_u$ - $(4)^3\Sigma^+_u$ and $D^1\Pi_u$ - $(1)^3\Delta_u$ S-O coupling element, which gave most satisfactory fit to experiment.

Finally the term ‘non-adiabatic’ dynamics is used to emphasize that the vibrational wavepacket dynamics is not a simple oscillation in a single, uncoupled electronic state. Such states arise when the B-O potential curves are well separated over the whole $R$-range of interest. For the case of a curve-crossing, the two extremes of very large or very small coupling element, also lead to simple adiabatic dynamics. In the first case, the wavepacket is making oscillations in one of the avoided crossing, adiabatic, potential curves, without leaking over to the other adiabatic state. In the second case, a very small coupling element implies that the two crossing diabatic states do not see each other, and the case is the same as for isolated states. The more complicated, challenging and interesting case is a curve-crossing with intermediate coupling strength, where in either the diabatic or adiabatic bases, the wavepacket will make transitions, split and interfere, that is performing ‘non-adiabatic dynamics’. Whether an intermediate coupling strength avoided crossing dynamics is described from adiabatic (with large non-adiabatic off-diagonal coupling) or diabatic (large electro-static off-diagonal coupling) zero-order representations is a matter of convenience.
4.1.3 Correlation diagrams

In the same adiabatic spirit as was used to obtain the potential curves of Fig 2.1, correlation diagrams, based on group theory, are useful in determining which atomic fine-structure level (spin orbit splitted) a certain molecular potential curve adiabatically dissociates into. This knowledge is important for the detection step, which involves the fluorescence from excited dissociated atoms. The dissociation process is assumed slow, enabling the electronic cloud to adjust to equilibrium for each R-value. An example of such a calculation is given in the appendix, where I show that the adiabatic dissociation limit of the $^3\Pi_g$, the final level of the A state experiment, is $5P_{3/2}+5S_{1/2}$.

4.2 General vibrational wavepacket theory

The depth of the theory presented here is kept to a minimum considering our specific experimental conditions:

1) The near-effusive beam (see chapter 3) produces a collision-free environment at the laser-molecule interaction point, meaning that we have no collision interactions. And self-absorption of the fluorescence in the detector direction is also negligible. Thus, the total signal detected is the statistical sum of the contribution of each molecule. Further, on the timescale of the pump-probe process ($t < 50$ ps), the spontaneous radiative decay of the excited electronic states ($t > 30$ ns) is also negligible. Altogether, this allows us to work with wavefunctions as a simpler alternative to the density matrix, since each molecule is independent of the others, and the measured signal is the incoherent sum of contributions from each molecule.

2) The electric field strengths of the pump and probe laser pulses are weak (not focused) at the laser-molecule interaction point. For the analytical treatment here, perturbation theory is used. Thus, the laser strength is kept low, in order to avoid effects such as Rabi-flopping [18], distorted wavepackets and in the extreme, distorted molecular structure (potential curves).

3) Magic angle condition. In chapter 4.3, I will demonstrate how, under certain conditions, the influence of the rotation part of the nuclear wave function can be greatly reduced. These conditions are a) linearly polarised pump and probe beams, with the magic angle, 54.7 ° in-between the electric fields b) isotropic detection proportional to final state population. As will be discussed later on, we approximately fulfil condition b) and condition a) was used for the measurements concerning the vibrational dynamics study. The remaining influence of rotation, even at magic angle, is a centrifugal correction to the potential curves, and a degeneracy factor for the thermal average.

4.2.1 Analytical model and classical arguments

Introducing the concept of the vibrational wavepacket in a diatomic molecule, a most simple model is used for a qualitative analytical treatment. Three electronic states are involved, a starting ground state $\Psi_g$, an intermediate state $\Psi_e$ (which is the state we wish to study), and a final state $\Psi_f$ (to which we probe the intermediate state
wavepacket after a time delay, \( \tau \). The laser pump pulse couples the ground and intermediate state, while the probe pulse couples the intermediate and final states. The laser pulses are assumed weak and separated in time. Thus, coherent pump-probe contributions around delay time \( \tau = 0 \) are ignored.

The width in energy of the wavepacket cover several discrete quantum states. It will therefore have semi-classical properties, following semi-classical trajectories in simple cases.

**a) Creation of vibrational wavepacket expanded in eigenstates**

The time axis of the pump-probe process is defined as shown in Fig 4.1.

![Fig 4.1 Time axis of the pump-probe sequence.](image)

- The time axis of the pump-probe sequence is defined as shown in Fig 4.1.
- The time \( t = 0 \) is well before the laser pump pulse arrives.
- The starting point is a molecule sitting in a vibrational level, \( i \), of the ground state, \( g \),

\[
\Psi_g(R,t) = C_i^g(t) \chi_i^g(R)
\]  

(4.4)

where \( \chi_i^g(R) \) is the steady state vibrational eigenfunction.

Perturbation theory assumes weak fields, leaving the ground state essentially unaffected by the pump pulse, with solution to eq. (4.9) below,

\[
C_i^g(t) = e^{-i\omega_g t}
\]  

(4.5)

Next, the molecule will be exposed to the laser pump pulse at time \( t_1 \) given by
\[ E(t) = E_0 \ e^{-\frac{(t-t_0)^2}{\Delta}} \ \cos(\omega_L t) = \frac{E_0}{2} \ e^{-\frac{(t-t_0)^2}{\Delta}} \left( e^{-i\omega_L t} + e^{i\omega_L t} \right) \quad (4.6) \]

\( E_0 \): amplitude
\( \Delta \): time width
\( \omega_L \): laser center frequency

Along the derivations, the rotating wave approximation will be applied, which neglects one of the \( \exp(\pm i\omega_L t) \) terms which leads to a highly oscillating term that is averaged out to zero.

The pulse is assumed nonchirped, but a chirp could easily be incorporated into \( E(t) \).

Due to the energy width of the pump pulse, where the energy spectrum is given as the Fourier transform of the temporal pulse shape, a multiple of vibrational levels, \( n \), of the excited state, \( e \), will be coherently populated. We may expand the excited state into vibrational eigenstates,

\[ \Psi_e(R,t) = \sum_n C_n^e(t) \chi_n^e(R) \quad (4.7) \]

and \( \chi_n^e(R) \) satisfies the time-independent Schrödinger equation (4.1) for the excited state,

\[ \left[ T_N + U_e(R) \right] \chi_n^e(R) = \hbar \omega_{en} \chi_n^e(R) \quad (4.8) \]

where \( T_N \) is the kinetic operator \( \propto \frac{d^2}{dR^2} \) and \( U_e \) is the excited potential energy curve.

The time-dependent Schrödinger equation for \( \Psi_e(R,t) \) including the electro-magnetic dipole interaction with the ground state, \( \Psi_g(R,t) \), has the following form,

\[ i\hbar \frac{\partial}{\partial t} \Psi_e(R,t) = \left[ T_N + U_e(R) \right] \Psi_e(R,t) + \mu_{eg} E(t) \Psi_g(R,t) \quad (4.9) \]

where \( \mu_{eg} \) is the electronic dipole moment (assumed \( R \)-independent) and \( E(t) \) is the time-dependent laser pump pulse electric field (assumed constant over the molecule geometric extent).

If the expansion for \( \Psi_e(R,t) \) is inserted and this equation and the equation multiplied by \( \langle \chi_n \rangle \) from left, using Dirac notation from now on, we obtain,

\[ i\hbar \frac{\partial}{\partial t} C_n^e(t) = \hbar \omega_{en} \ C_n^e(t) + \mu_{eg} E(t) \left\langle \chi_n^e(R) \right| \chi_i^g(R) \right\rangle C_i^g(t) \quad (4.10) \]

Solving this linear differential equation for \( C_n^e(t) \), together with the initial condition, all \( C_n^e(0)=0 \), and inserting the above expressions for \( E(t) \) and \( C_i^g(t) \), we finally have,
This is a quantum mechanical recipe of making a wavepacket in a simple one photon excitation from electronic ground state to a single excited electronic state.

Looking closer at the ingredients we note:
→ The electronic dipole moment, $\mu_{eg}$, together with the field strength, $E_0$, give the overall strength of the excitation.
→ The vibrational eigenfunction overlap, $\langle \chi_e^n(R)|\chi_g^n(R) \rangle$ (the absolute value square of this is the F-C factor), weights the individual amplitudes of the $C_n^e(t)$.
→ The term $e^{-i\omega_{n,e}t}$ is the free time evolution of the $C_n^e(t)$.
→ The integral gives the contribution (amplitude and phase) from the laser pulse characteristics. The integral is large when $\omega_{e,n}$ is on laser resonance, $\omega_\text{L} = 0$, and decreases as $\omega_{e,n}$ diverges from resonance.

Thus, equation (4.11) give the complex expansion coefficients of the excited wavefunction as a function of time under the assumptions taken above. To proceed, and looking at the shape and behaviour of the wavepacket, $|\Psi_e(R,t)|^2$, specific input data, e.g laser pulse characteristics, vibrational levels $\omega$, vibrational eigenfunctions $\chi$, need to be available, and eq. (4.11) may be solved numerically. We postpone this to the chapter 4.2.2.

However, since the wavepacket, with its manifold of vibrational wavefunctions, have partly classical behaviour, some insight is given from classical trajectory laws:

Energy and momentum conservation $\Rightarrow$ a wavepacket will have the highest probability to be excited at a position $R$ when the difference potential, $\Delta U = U_e - E_g$, equals the center laser pulse energy, $E_\text{L} = \hbar\omega_L$. If this occur for a single $R$-value within the reach of the wavepacket being pumped, the probe-point is well defined.

For an ideal case of a molecule, residing in $v = 0$ of the ground state, being resonantly excited by a short enough, non-chirped, laserpulse, the created wavepacket is approximately an excited replica of the ground state wavepacket $|\Psi_g(R,t)|^2$ (vertical transition), being in a non-stationary state (and with less amplitude in the perturbative region) [28]. In this case, the nuclei don’t have time to move during the excitation. For a general case, however, the excited wavepacket may look quite different to the ground state wavepacket [28].

b) Propagation of vibrational wavepacket

The propagation of the created, excited, wavepacket is automatically taken care of in eq. (4.11), via the $e^{-i\omega_{n,e}t}$ term. As $t$ increase after the laser pump pulse, the integral stays constant (electric field amplitude is zero) and each vibrational component, $n$, performs free time evolution. This continues until the laser probe pulse arrives. As for the creation of the v.w.p, propagation will be illustrated in chapter 4.2.2.
c) Probing of vibrational wavepacket

As a means of observing the wavepacket propagation, another laser pulse, the probe, induces a transition to the final state after a time delay $\Delta t$ after the pump pulse. Conserving energy and momentum again, the transition takes place at the value $R$, where the difference potential matches the probe frequency, $\omega_{pr}$. The probe laser couple two electronic states. The detection signal, fluorescence, is assumed proportional to the final state population.

If we assume non-overlapping pump and probe pulses, the full pump-probe sequence consist of two sequential linear (weak fields) excitations [29]. Same procedure as deriving eq. (4.11) can be used for the probe step. The times for the probe step is noted by primes. Time zero, $0'$, is now chosen inbetween the laser pulses, and the wavefunctions expanded in vibrational eigenstates, where the excited state act as ground state and the final state act as excited state. At the new ‘time zero’, the initial values of the intermediate state coefficients are given by eq. (4.11), while the final states coefficients are all $C_m'(0)=0$. The expression for the $C_m'(t')$ will be a sum of integrals of the same form as eq. G.F, where the summation is over all participating intermediate state vibrational components.

The final state population, after the probe pulse interaction, is the sum of all $\left|C_m'(t')\right|^2$, which is the same as the trace of the density matrix of the final electronic state. The final state population can be read off by e.g. fluorescence measurement (if it is isotropic with no angular dependence, see chapter 5.3.1). In the Rb$_2$ cases studied in this thesis, the final state dissociate into excited Rb atoms (one excited and one ground state atom for each Rb$_2$) and their fluorescence as they decay is our measured signal.

4.2.2 Numerical approach and simulation

Running our simulation program on the simple A-state system substitute, the harmonic model system, serves several purposes: first, it enables me to illustrate graphically the basic concepts of wavepacket theory as a background to the more complicated non-adiabatic dynamics. Second, the well known results from harmonic potentials make these simulations a great test of the program reliability and correctness. In the beginning, the $b^3\Pi_u$ will be turned off (by setting $V_{SO}=0$), and the simple dynamics can be classified as adiabatic. At the end, $V_{SO}$ is turned on to intermediate strength, including the $b^3\Pi_u$ state, and we will have the first taste of non-adiabatic dynamics.

Solving eq. (4.11) numerically in practice, for a more complicated system at hand, is quite troublesome, since it rests on the determination of energy levels and eigenstates. Instead, another approach has been used for the numerical simulations. The electronic wave functions are not expanded in vibrational eigenstates, and eq. (4.9) is used directly, where the potential curves, $U_N(R)$, act as a driving force on the wavepackets.

The model now contains four potential curves, where the two intermediate states cross and are approximated with harmonic potentials, as was outlined in chapter 2.2. They
will be used throughout this chapter, where the A state and b state are always substituted with their corresponding harmonic potential curves. Apart from the harmonic simplification, the model describe the Rb$_2$ A state system. Within the model of this general wavepacket introduction, the S-O coupling element between the A and b state (the harmonic substitutes) will first be set to zero and later turned on. For the real Rb$_2$ simulations, the S-O coupling is always there (as it is for the real molecule, using the diabatic S-O basis). For the wavepacket excitation process, the influence of the b state is small since the optical transition only couples the singlet ground state with the singlet A state, and the crossing point is quite remote.

The wavefunctions and potential curves are discretised in R, and contained in vectors of size 2047. Eq. (4.9) is then solved numerically, propagating the wavefunctions, using the split operator Fourier transform method.

a) Simulation techniques

I) Split-operator Fourier transform method

A formal solution of the time-dependent Schrödinger equation over a time step $\Delta t$ is,

$$\Psi(R,t+\Delta t) = \exp[-i\Delta t(T_N+U(R,t))/\hbar]\Psi(R,t)$$ (4.12)

if $U(R,t)$ is approximately constant over the time interval $\Delta t$.

$\Psi$ here is the overall total wavefunction, and may be expanded in electronic states. $T_N$ is a kinetic energy operator sitting on the diagonal in a matrix representation. $U(R,t)$ contains the electronic potential-curves on the diagonal, and couplings on the off diagonal elements. The couplings may be internal, e.g. S-O coupling (time-independent) or external, e.g. optical interaction by laser pulses (time-dependent). The time dependence of $U$ is stepwise, it stays constant within $\Delta t$, but may change inbetween steps. Expanding the exponential into first order Taylor expansion gives a numerically unstable solution [16].

The split-operator method consist of splitting the exponential into, at least, two product terms,

$$\exp(A+B) \approx \exp(A)\exp(B), \text{ or to higher, second order accuracy:}$$

$$\approx \exp(A/2)\exp(B)\exp(A/2)$$ (4.13)

since the A and B operators in general do not commute. In the simulation code, the first of these approximations is used between the kinetic, $T_N$ and potential, $U(R,t)$ operators. The second, higher order approximation, is used to split up the potential operator between potential curves, and between couplings. By using this split technique, any number of potential curves and couplings between any states, are broken down into pairs of states where analytical solutions exist. The method is approximate, and depends on using short enough time steps. Convergence is checked by reducing the time step.

The kinetic exponential propagation is solved by using a trick, the fast Fourier transform. The $d^2/dR^2$ term in the exponential is quite troublesome, since it is not
diagonal in R, or in other words, at least three R values of the wave function is necessary for a second derivative. The trick is to go over to momentum space by taking the Fourier transform of $\Psi$, multiply by a diagonal matrix $\propto \exp(p^2)$, and inverse Fourier transforming back. The potential 2x2 matrix exponential propagator can analytically be transformed to a 2x2 matrix by diagonalisation.

(II) molecular rotation

Molecular rotation is included as an additional term $\propto J(J+1)/R^2$ ($J \gg \Omega$, the angular projection on the inter nuclear axis) to all potential curves on the diagonal of $U(R,t)$ [24]. Optical transitions, following selection rules on $\Delta J \pm 1$ or 0 [30], may couple different J’s, but this is ignored, since a unit change in J has a small effect on the vibrational wavepacket dynamics. Here, $\Delta J$ is always zero, and the excitation probability is contained in the statistical factor $(2J+1)$ [30].

(III) numerically calculated vibrational eigenstates of the electronic ground state

Ground-state vibrational wavefunction and energy-level is calculated using the Lanczos method [31], for any $v$ and $J$ level ($J$ included in the potential curve). In short, the method consist of building up an orthogonal basis using Gram-Schmidt orthogonalisation, starting from an initial, guessed, basis function. It is done in such a way as to transform $H$ into tri-diagonal form, from which eigenvalues and eigenvectors are obtained by diagonalisation. Off-diagonal elements are couplings of the form $<1|H|2>$, which couple the initially, poorly guessed, basis functions. The larger the basis-set created, the better the approximation become.

(IV) thermal averaging

Thermal average is finally obtained by summing over $J$ and $v$ of the ground state, where each signal time-trace $\{v,J\}$ is weighted with the Boltzmann factor,

$$(2J+1) \exp(-E_{v,J}/k_B T) \quad (4.14)$$

where

$(2J+1)$ is the rotational degeneracy ($M_J$)

$E_{v,J}$ is the energy of the level $\{v,J\}$ in the ground state

$k_B$ : Boltzmann constant

$T$ : temperature ( $T=700$ K in the simulations)

Coherences between rotational levels, $J$ are not present in magic angle measurements [32].

The above features have been utilised so far on the A state system, and for the numerical illustrations of the general wavepacket dynamics presented here. For the earlier analysis of the D state system, a simpler program was used available at that time. It was also based on the split-operator Fourier transform method, but of less refinement.
b) Creation of vibrational wavepacket

For better visualisation of the excitation process, eq. (4.9), together with a unitary transformation \( \Psi_g(R,t) = \exp(+i\omega_L t) \Psi_g(R,t) \), may be put in matrix form [16],

\[
\begin{bmatrix}
\frac{i\hbar}{\partial t} \Psi_e(R,t) \\
\Psi_e(R,t)
\end{bmatrix} =
\begin{bmatrix}
T_N + U_e(R) + \hbar \omega_L & V_{EM} \\
V_{EM} & T_N + U_e(R)
\end{bmatrix}
\begin{bmatrix}
\Psi_g(R,t) \\
\Psi_e(R,t)
\end{bmatrix}
\]

(4.15)

where,

\[
V_{EM} = \mu_{eg} E_0 e^{-\frac{(t-t_0)^2}{\Delta^2}}
\]

(4.16)

In all numerical simulations, the pump pulse is centred at \( t_0 = 0 \), and the propagation start at \( t = -250 \) fs. The laser pulse intensity FWHM is 120 fs. Initially, the excited wavefunction, \( \Psi_e \) is zero and \( \Psi_g \) is a steady state vibrational eigenfunction in the ground state. The S-O coupling to the b state is set to 0, thus \( \Psi_e \) belongs to the A state solely.

We see that the lower potential curve is simply shifted up an amount \( \hbar \omega_L \) by the laser and the laser induced transition appears as a curve-crossing, where the coupling \( V_{EM} \) (here assumed weak), transfers wavefunction between the electronic states while the laser pulse is on. Fig 4.2 shows some examples of the created wavepacket just after the pump-pulse excitation. For comparison, a (theoretical) FWHM = 7 (\( \Delta t \)) fs pump pulse shows an ‘ideal’ excitation.

![Fig 4.2 Creation of excited state wavepacket](image)

Fig 4.2 shows that the ideal picture of the excited wavepacket being a smooth replica of the \( v = 0 \) ground state wave function is strictly only valid for very short laser pulses.
on resonance. But even for the worst case of Fig 4.2, the created wavepacket is localized and will make oscillations following approximately the classical trajectory (Ehrenfest’s theorem), although it will breath and have a rather spiky shape. This permit us to use wavepacket semi-classical trajectory explanations of the A-state system experiments, even for higher ground state vibrational levels than zero. Note the four steady state peaks of the \( v = 3 \) ground state wavefunction amplitude. The energy width of the pump pulse is inherent in its time width, where the two are connected via a Fourier transform.

Fig 4.2 also indicate the broadening of the created wavepacket as the pump pulse time width increases, since the wavepacket starts to propagate during the pulse [28]. If the pump pulse is long enough, during the pulse, the excited wavepacket will spread out over the whole excited potential curve, interfere with itself, and relax into a steady state wavefunction. If such artificially long pump pulse is used instead in the simulation of Fig 4.2 c), the excited wavefunction has 8 nodes, meaning that \( v = 8 \) is excited, at an energy of about 390 cm\(^{-1}\) from the bottom of the excited state. This also illustrate the connection between time and frequency domain spectroscopy.

c) Autocorrelation of the propagating vibrational wavepacket

As a means of connecting the time and energy views of the wavepacket, the autocorrelation may be used and is defined as:

\[
a(t) = \langle \Psi(0) | \Psi(t) \rangle
\]  

(4.17)

It is the overlap integral of the wavepacket at time \( t \) with the same wavepacket at an earlier time \( t=0 \). Note that if the system is closed, with no interaction to the surrounding (e.g no decay), the time \( t = 0 \) is arbitrary (after the pump pulse), and \( a(t) \) depends only on the time range \( t-t(0) \). Taking the Fourier transform of \( a(t) \), \( A(E) = f(a(t)) \), gives the energy spectrum of the wavepacket \( \psi(t) \). This can be illustrated by expanding the wavepacket \( \psi(t) \) in eigenstates:

\[
| \Psi(t) \rangle = \sum_n c_n | n \rangle e^{-iE_n t / \hbar}
\]

(4.18)

\[
a(t) = \sum_n | c_n |^2 e^{-iE_n t / \hbar}
\]

(4.19)

And \( A(E) \) gives \( |c_n|^2 \) as a function of \( E_n \). Since \( |c_n|^2 \) represent population and \( E_n \) the energy eigenvalues of the potential, \( A(E) \) tells us 1) the positions of the energy eigenvalues, \( E_n \) (covered by the pump pulse). 2) which eigenstates are populated and to what extent.

Alternatively, the absolute value squared of the autocorrelation may be used, and it’s Fourier transform gives the ‘energy difference’ spectrum (or rather the square of the product of coefficients) of the involved levels of the wavepacket.

\[
b(t) = \left| \langle \Psi(0) | \Psi(t) \rangle \right|^2
\]

(4.20)
and using the same expansion as above gives:

\[
b(t) = \left( \sum_m |c_m|^2 e^{i(E_m t)\hbar} \right) \left( \sum_n |c_n|^2 e^{-i(E_n t)\hbar} \right) = \sum_{m,n} |c_m|^2 \cdot |c_n|^2 e^{i(E_m - E_n)t/\hbar} \quad (4.21)
\]

The Fourier transform of \(b(t)\), \(B(E)\), now gives \(|c_m|^2 |c_n|^2\) as a function of \(E_m - E_n\).

Let us apply these methods to investigate propagation and frequency content of the excited wavepacket, \(\psi(t)\), propagated by the split operator technique.

When the pump-laser interaction is over, the excited wavepacket propagates on the excited state, according to eq. (4.15), which state may be coupled to other excited states. In our Rb\(_2\) system, this is the case, and an additional excited state has to be added to eq. (4.15) which couples via \(V_{SO}\) (which can be quite large) the two excited states. As a start, \(V_{SO}\) is set to zero, and we take a look at the propagating excited wavepacket in a single state (a single intermediate potential curve). Thereafter we will turn on \(V_{SO}\) and look at the effect of two intermediately coupled excited states.

We choose as the starting point \(v = 3\) vibrational eigenfunction in the ground state, \(X^1\Sigma_g\). At \(t = 0\), a pump laser (120 fs FWHM, \(\lambda_{pump} = 910\) nm) excites a wavepacket in the unperturbed A state. The excited wavepacket will perform simple harmonic oscillations, although the shape of the wavepacket may vary periodically, called breathing, see Fig 4.3. If the width of the excited wavepacket is smaller than the width of the \(v = 0\) steady state wavefunction of the excited state, it will broaden in the centre of the potential curve, and vice versa.

![Fig 4.3](image)

**Fig 4.3**  a) Contour plot of ground state (green) and excited A state (purple) wave functions using \(\lambda_{pump} = 910\) nm, as a function of time and inter-nuclear distance, \(R\). Time zero is at the centre of the pump pulse. The pump laser pulse burn out a hole from the ground state wavefunction, initiating an oscillating wavepacket in the ground state as well as in the excited state. Due to the higher energy level of the wavepacket in the A state, the oscillation amplitude is larger than for 940 nm excitation. b) Fourier transform of the autocorrelation, \(A(E)\), of the excited wavepacket in Fig 4.3 a) (purple). The horizontal axis is energy (cm\(^{-1}\)), where zero corresponds to the minimum of the A-state potential curve.
Notice the ground state wavepacket, created from the larger excitation probability. The excited state wavepacket is not beautifully gaussian (mostly due to the non-gaussian shape of \( v = 3 \) in the ground state), but still fairly localised. It undergoes heavy breathing as well as oscillation. The excitation process is still not a ‘vertical copy’, as is also reflected in the oscillation of the created wavepacket in the ground state. The maximum peak in the Fourier transform of the autocorrelation (\( A(E) \), Fig 4.3 b)) is the \( v = 8 \) level of the A-state. The autocorrelation is taken over a time range of 4.5 ps.

The longer the time range of the autocorrelation, the higher the energy resolution becomes. This shows that at really short time scales after the pump pulse, the eigenstates are not well-defined, and the expansion in vibrational states in the analytical treatment of the wavepacket is not unique. Only when the wavepacket has lived for some time and traced out an autocorrelation function, the energy levels and corresponding eigenstates becomes known. Still, nothing prevent us from making the expansion of the wavepacket in an eigenstate basis, valid from delay time zero.

The smaller the time steps of the autocorrelation, the larger is the range of energy in the energy spectrum.

Further, Fig 4.3 b) shows that we populate about three vibrational levels within the wave packet’s FWHM of about 120 cm\(^{-1}\). The levels are equidistant as expected for a harmonic potential energy curve. Note that the vibrational levels seen in Fig 4.3 b) are only the ones the wavepacket populates.

Now, we include the b state and turn on the SO coupling, \( V_{SO} = 66 \text{ cm}^{-1} \) (splitting the wavepacket into two equal size components at the first crossing passage), Fig 4.4. Pump FWHM = 120 fs and \( \lambda_{\text{pump}} = 910 \text{ nm} \):
The energy levels are now perturbed and we can investigate their sensitivity by changing coupling strength to $V = 76 \text{ cm}^{-1}$ in Fig 4.5 a) or shift the b state by only 100 cm$^{-1}$, Fig 4.5 b).

![Image](image_url)

Fig 4.5 a) slightly changed coupling strength to $V = 76 \text{ cm}^{-1}$. b) slightly shifted b state by 100 cm$^{-1}$.

Fig 4.5 is quite different to Fig 4.4. Thus, the energy levels are very sensitive to e.g. the quality of potential curves at intermediate strength coupling. Also the exact value of the coupling element influences individual energy levels and the created wavepacket. The energy levels seem to be randomly distributed, but as we will see, a more collective approach, the wavepacket creation and dynamics will show structure of energy levels, and it’s behaviour is not random. However, some uncertainties do remain, e.g. the ‘phase’ of the interference behaviour.

The uncertainties of the energy level positions will restrict the analytical density matrix, state multipole, modelling of the anisotropy, introduced in chapter 4.3.

If $V_{SO}$ was 10 times lower or 3 times larger, the motion seen is ‘adiabatic’ (equidistant energy levels, either in the upper adiabatic potential (high $V_{SO}$) or in the diabatic A state (low $V_{SO}$)) and a shift of b of 100 cm$^{-1}$ does not effect the energy levels, more than an overall shift for the high $V_{SO}$ case.

d) Probing of vibrational wavepacket: the Rozen-Zener model

The straightforward way to include the probe process is to add the final state to eq. (4.15) [16], shifted down by the probe frequency and optically coupled to one of the excited states. The probe interaction is treated as a curve-crossing, just as the pump interaction was. The final state population is then simply the norm of the final state wavefunction.

This method is unfortunately quite time-consuming when a scan of different pump-probe delay times is performed. For each delay time, the probe interaction propagation has to be recalculated, since the previous delay time probe interaction destroyed the intermediate level wavefunction. Then it is appealing to use an
approximation of the probe step, which does not affect the intermediate wavefunction. For this purpose we use the Rosen-Zener pulse model [16].

This model freezes the propagation of the wavefunctions at different delay times and gives an expression for the final state population. The intermediate level wavefunction is sliced up in R (the wavefunction at different grid-points) and each slice is assumed to be excited independently of the others. The contribution from each slice to the final state contribution is,

$$P(R, \tau) = \sin^2(\pi V_0 T/2.63) \text{sech}^2(\pi \delta(R) T/(5.26) |\Psi_e(R, \tau)|^2$$ (4.22)

$V_0$: amplitude of the coupling term.
$T$: FWHM of probe laser pulse
$\delta(R)$: local detuning, $(U_f - U_e) - \omega_{pr}$

And the total population at delaytime $\tau$ is the sum of $P(R, \tau)$ over R.

The first term in eq. (4.22) take into account Rabi-flopping if the field is strong, which it is not in our case. The second term gives the radial probability of excitation. It is large for a small argument and approaches zero with increasing $|\delta(R) T|$. It therefore sets up an R window on the intermediate, probed state. The final signal is proportional to the amount of wavefunction therein. The main effect of the window width is to smoothen out the signal time structure, but within realistic pulse widths, the sensitivity is small. This model is valid if the probe is much shorter in time than the period of the vibrating wavepacket, that is the wavepacket must not move during the probe process. As the probe position is close to the outer turning point of the b state, the wavepacket moves relatively slowly in that region, and the model is expected to be satisfactory. It is our intention to make a comparison, in the near future, with full probe time-propagation to check the accuracy of the Rozen-Zener model for our specific molecular system. Note the limiting factors of the probe pulse time width $T$.

If $T$ is too small, we loose localization of the probe point, hence any R value is probed with the same probability. If $T$ is too large, we loose time resolution and the signal is averaged out in time (besides the frozen approximation goes wrong).

### 4.3 General rotational wavepacket theory

The following conditions will be assumed: The Rb$_2$ molecules are in a collision-free environment, the natural decay is neglectable on our time scale ($\tau < 30$ ps), laser beam intensities are low and they are perfectly linearly polarised. The laser pulse time width is neglected and treated as a delta pulse, since the pulse width, FWHM $\approx$ 120 fs, is much smaller then the rotational period, $T_{rot} \approx$ 5 ps at $J=100$.

To start with, vibration is neglected and a simple $\Sigma - \Sigma - \Sigma$ case will be treated, where $\Sigma$ means that the electronic angular momentum’s (L) projection on the inter-nuclear axis is zero. In a $\Sigma - \Sigma$ transition, as for both pump and probe transitions, the transition dipole moment, $\mu_{12}$, is parallel to the inter-nuclear axis (only diatomic molecules are treated here). The optical selection rule is $\Delta J = \pm 1$. Before the laser pump pulse arrives, the molecules’ axis, or equivalently their transition dipole moments in this case, are randomly oriented in space. The linearly polarised pump pulse will
preferably excite those molecules having their transition dipole moments (or axis) parallel to the electric field. Thus, the pump pulse creates a non-isotropic distribution of excited molecules (and also remaining non excited molecules) with respect to their transition dipole moments (or axis) orientations. The probe pulse is then used to analyse the remaining anisotropy after a delay time, $\tau$, during which time the diatomic molecules will rotate around an axis perpendicular to their inter-nuclear axis.

4.3.1 Semi-classical model

At time zero, the pump laser excites a molecular axis (or transition dipole moment) distribution according to [36],

$$I(\theta, t = 0) \propto \left| \mu_{12} \cdot E \right|^2 = (\mu_{12} \cdot E)^2 \cdot \cos^2(\theta)$$  \hspace{1cm} (4.23)

where $\theta$ is the angle between the dipole moment and the electric field.

As the excited molecules start to rotate, this distribution, for a single molecule starting from rotation level $J$ in the ground state, will change in time according to [37],

$$I(\theta, t) \propto \frac{1}{3} \left[ 1 + \beta \left( \frac{3 \cos^2 \theta - 1}{2} \right) \right]$$  \hspace{1cm} (4.24)

$$\beta = 0.5 + 1.5 \cos(\omega_J t)$$

$$\omega_J = 2\pi (4J+2)B_e$$

$\beta$ and $\omega_J$ are taken from quantum mechanics, where $\omega_J$ is the energy difference between the coherently excited $J+1$ and $J-1$ levels. This expression is valid in the classical limit, $J \rightarrow \infty$. However, already at $J = 5$ the deviation from quantum theory (see chapter 4.3.2) is less than 1%. Fig 4.6 shows the axis distribution at different times.

Fig 4.6 Angular distribution of excited molecule axis at time a) $t = 0$, b) $t = T_{rot}/8$, c) $t = T_{rot}/4$. The small arrow in all figures illustrate the constant, time-independent distribution value in the magic angle, $\theta_m$, direction.
The rotation manifests itself as a wobbling of the distribution between a dumbbell and a doughnut shape. The norm of the distribution is conserved in time. After \( t = T_{\text{rot}}/4 \) the sequence reverses, and at \( t = T_{\text{rot}}/2 \), the distribution is identical to Fig 4.6 a), where the molecule has turned 180 degrees. Note the specific angle \( \theta_m = \arccos \left( \frac{1}{3} \right)^{1/2} = 54.7^\circ \) in which the distribution value is constant, or time-independent. This angle is called the magic angle. At this angle we always have the same number of molecules, or loosely speaking, as many molecules turn into this angle as turn away.

When including the probe laser pulse, the relative E field orientations are important. The probe will always have its E-field along the z-axis (vertical), while the pump electric field can be turned in the z-y plane. The dumbbell-doughnut distribution of excited molecules by the pump, will thus be tilted an angle \( \theta_r \) from the z axis and have the general expression,

\[
I(\theta, \phi, t) \propto \frac{1}{3} \left[ 1 + \beta \left( \frac{3}{2} \sin(\theta) \sin(\phi) + \frac{1}{2} \cos(\theta_r) \cos(\theta) \right)^2 - 1 \right]
\]  

(4.25)

where \( \theta \) is the angle from the z axis, \( \phi \) is the angle from the x axis (direction of laser beam propagation), \( \theta_r \) is the pump pulse E-field tilt angle from the z axis in the z-y plane, and \( \beta \) as given above.

The final state axis distribution, immediately after the probe laser-molecule interaction, is obtained by weighing eq. (4.25) by a \((\mu_{12} \cdot E)^2 \cdot \cos^2(\theta)\) factor (see eq. (4.23)). The norm of the final state axis distribution is proportional to the number of pump-probe excited molecules to the final state. If we for now assume the detection to be isotropic, integrating the final state distribution over \(4\pi\) solid angle (the norm) give us the detected signal. Solving the integrals for the norm of the final state analytically, the detected signals are given by,

\[
S_{||} = C(2 + \cos(\omega_r t))
\]

\[
S_\perp = C\left( \frac{3}{2} - \frac{1}{2} \cos(\omega_r t) \right)
\]

\[
S_m = \frac{1}{3}(I_{||} + 2I_\perp) = \frac{5}{3}C
\]

(4.26)

for the parallel \((\theta_r = 0^\circ)\), perpendicular \((\theta_r = 90^\circ)\) and magic angle \((\theta_r = 54.7^\circ)\) respectively. Note that, as for the intermediate state axis distribution, the magic angle pump-probe signal is time-independent.

If we expand the model to include isotropic, time-dependent and J-independent vibration signal, \(A(t)\), all equations of (4.26) are multiplied by \(A(t)\) [38] (rotation and vibration are assumed separated for each molecule). Defining the anisotropy as [39],

\[
R_d(t, J) = \frac{S_{||}(t, J) - S_\perp(t, J)}{S_{||}(t, J) + 2S_\perp(t, J)}
\]

(4.27)
for molecules excited from a single ground state rotational level J. The isotropic signal \( A(t) \) cancels and the denominator is the isotropic, time-independent rotational signal. As the rotational dynamics of the intermediate state is cylindrically symmetric with respect to the pump-pulse electric field axis, only two measurements are necessary to find out the non-isotropic intermediate state axis distribution, namely \( S_\parallel \) and \( S_\perp \). The ultimate range of \( R_{\lambda}(t,J) \), ignoring the distributions, is +1 (all molecules exactly aligned along the pump E-field axis) and −1/2 (all molecule exactly in a plane \( \perp \) to the pump E-field axis). \( R_{\lambda}(t,J) = 0 \) means a totally isotropic intermediate state axial distribution. In the case of the molecular \( \Sigma^-\Sigma^\pm\Sigma^- \) transitions, due to the spread of the axial distributions, \( R_{\lambda}(t,J) \) range between 0.4 (molecules aligned with the pump) and −0.2 (molecules perpendicular to the pump). Inserting eq. (4.26) into eq. (4.27) we get,

\[
R_{\lambda}(t,J) = \frac{1}{10} (1 + 3 \cos(\omega t))
\]  

(4.28)

The anisotropy, \( R_{\lambda} \), as defined by eq. (4.27) has a direct physical meaning in a three dimensional system, of cylindrical symmetry around the pump E-field axis. Namely, it tells how random, or organized, the intermediate-state molecular axis’s orientations are. In addition to the anisotropy, the polarisation, \( P \), is defined as [39],

\[
P = \frac{S_\parallel - S_\perp}{S_\parallel + S_\perp}
\]

(4.29)

which have direct physical meaning in a two dimensional system, e.g. the degree of polarisation of the electric field in a laser beam, in a plane perpendicular to the propagation direction. In this example, \( S_\parallel \) is the signal measured after a polarising filter parallel to the main E-field axis, and \( S_\perp \) the signal measured with polarising filter turned 90° to the main E-field axis.

The thermal average of \( R_{\lambda} (t, J) \) is obtained from eq. (4.27) if the signals, \( S_i \), are averaged over the Boltzmann ground state distribution,

\[
S_i(t,J) = \sum_j P_j S_j(t,J) A(t)
\]

(4.30)

where \( P_j = (2J + 1) \exp(-B_0J(J+1)/k_B T) \)

\( B_0 \) is the rotational constant evaluated at equilibrium inter-nuclear distance. The \( J \)-independent isotropic factors \( A(t) \) cancel when the signals, \( S_i \) are inserted in eq. (4.27), and the result is equivalent to that one would get if the average is done directly over \( R_{\lambda}(t,J) \) instead of over \( S_i(t,J) \). The average \( R_{\lambda}(t) \) will then contain many terms of the form of eq. (4.28) with different \( \omega \)’s. At time \( t = 0 \), \( R_{\lambda}(t=0) = +4/10 \). As \( t \to \infty \), the cosine terms dephase and average out to zero, giving \( R_{\lambda}(t=\infty) = +1/10 \). \( R_{\lambda}(t) \), the thermal average of the pure rotation anisotropy in a \( \Sigma^-\Sigma^-\Sigma^- \) case, is plotted in Fig 4.7, with parameters valid for the experiment on the Rb\(_2\) A-state system.
Interestingly, the thermally averaged anisotropy does not decay to zero for large times, but remains at a value of $+0.1$, assuming that no collisions occur and $\bar{\mathbf{J}}_{\text{tot}}$ (total angular momentum $= \mathbf{J}_{\text{tot}} + \bar{\Omega}$) remains constant in time. This ‘favouring’ of the parallel signal for the thermal average, can be understood from a simple picture: all excited intermediate state molecules, regardless of $J$, start from a dumbbell distribution along the pump electric field. As time goes on, each molecule will rotate, perpendicular to its axis, with an angular velocity set by $J$. After the molecule rotates half a period, it is back to being aligned with the pump electric field direction, and will have a maximum probe probability for parallel pump-probe. Same goes for all molecules. For the perpendicular probe direction, only half of the originally excited molecules will rotate into the probe electric field direction for maximum probe probability. Therefore the parallel signal will remain larger than the perpendicular signal, giving a net positive anisotropy.

### 4.3.2 Full quantum mechanical model

The same simple system of $\Sigma$-$\Sigma$-$\Sigma$ transitions will now be treated fully quantum mechanically using the density matrix. The benefit with the density matrix approach is that we may collectively treat all projections $M$ of the total angular momentum $\mathbf{J}$ onto a $z$-axis (defined by the laser electric field). This will enable us to define state-multipoles [40], which have direct physical meanings, such as orientation and alignment. Many of the following formulas are taken from the book of Blum [40]. Using symmetry considerations, many possible state-multipoles are zero, and the calculation load can be greatly decreased. In addition, state-multipoles are easily rotation transformable, and the axis distributions are straightforward to extract. The state-multipoles and density matrix can be transformed into each other, and the information content is identical. For the laser-molecule interaction steps, and the time propagation, the density matrix is suitable. For the rotation of coordinate frame (through the angle between pump and probe E-fields) and extraction of axis
distributions, the state-multipoles are suitable. Again, we shall assume that the final signal is proportional to the final state population.

The statistical density operator is defined as,

\[ \rho = \sum_n W_n |\Psi_n\rangle \langle \Psi_n| \]  

(4.31)

where \( W_n \) is the statistical weight of the wave function \( \Psi_n \). The density matrix elements are obtained by ‘sandwiching’ \( \rho \) between basis functions, \( \langle \phi_i \rho \phi_j \rangle \), where the \( \Psi_n \)'s are expanded in \( \phi_i \)'s as usual. For an isotropic, statistical, ensemble of molecules in the ground state, \( J = J_0 \), the starting density operator is given by,

\[ \rho_0 = \frac{1}{2J_0 + 1} \sum_{M_0} |J_0 M_0\rangle \langle J_0 M_0| \]  

(4.32)

that is, the density matrix is diagonal in \( M_0 \), with equal elements, reflecting the statistical, isotropic orientations of the molecular axis’s (the diagonal elements being the probability of finding the molecule with \( J = J_0 \) having projection \( M_0 \)). Statistical thermal averaging over \( J_0 \) is done at the end, in the same way as for the semi-classical calculations.

Excitation of the pump pulse, at time \( t = 0 \), results in the excited density matrix elements,

\[ \langle J' M_0 | \rho_{\text{out}} | J M_0 \rangle = \frac{A(\omega)}{2J_0 + 1} \sum_{M_0} |J' M_0\rangle \langle J_0 M_0| \langle J M_0| d_z |J_0 M_0\rangle^* \]  

(4.33)

where the selection rules of a linearly polarized electromagnetic excitation have been used,

\[ J',J \leq J0+1 \text{ or } J0-1 \]
\[ \Delta M = 0, K = 2 \text{ or } 0, Q = 0 \text{ in the state multipoles of the intermediate state.} \]

\( A(\omega) \) is a numerical factor depending on excitation probabilities (electric field strength \( \bullet \) transition dipole moment) apart from the purely geometrical term. It disappears in the, from now on, normalised \( \rho \). The dipole transition elements are obtained from,

\[ \langle \Lambda_1 J' M_0 | d_z | \Lambda_0 J_0 M_0 \rangle = \left[ (2J'+1)(2J_0+1) \right]^{1/2} \begin{pmatrix} J' & 1 & J_0 \\ -\Lambda_1 & -q & \Lambda_0 \end{pmatrix} \times \begin{pmatrix} J' \\ -M_0 \\ 0 \end{pmatrix} \langle \Lambda_1 | d_z | \Lambda_0 \rangle \]  

(4.34)

\( \Lambda_1 \) and \( \Lambda \) are the projections of \( L \) on the molecular axis of the electronic states, here both equal to 0 making \( q = 0 \) from symmetry properties of the 3J symbols [39]. The expression can be generalised, e.g. having different \( M' \), \( M \), and \( M_0 \) for non-linearly polarized light. For \( J \), the same expression applies if \( J' \rightarrow J \). Later on, the same
expression will be used for the probe transition, where \( J', J \) are then the final state quantum numbers, and \( J_0 \) takes the intermediate state \( J \) values, summed up one at a time using eq. (4.34).

The matrix elements with \( J' = J \) are diagonal terms giving the population of state \( J \). \( J' \neq J \) are off-diagonal coherence terms.

The corresponding state-multipoles are now calculated as,

\[
\langle T(J'J)_{KQ} \rangle = \sum_{M_0} (-1)^{J-M_0} (2K+1)^{1/2} \begin{pmatrix} J' & J \\ M_0 & -M_0 \end{pmatrix} K \langle J'M_0 | \rho | JM_0 \rangle
\] (4.35)

Both the density matrix elements and the state-multipoles can be straight-forwardly generalised to include several coupled intermediate electronic states, (the case of the A-state system) and are named \( \langle \Lambda'J'M' | \rho | \Lambda JM \rangle \) respectively \( \langle T(\Lambda'J'J)_{KQ} \rangle \).

We will use this in the chapter 5.3.2.

The axis distribution of the intermediate \( \Sigma \) state at time \( t=0^+ \), with laser pulse E-field in the z direction is obtained from,

\[
I(\theta, t = 0) = \langle Y_{00} (t = 0) \rangle Y_{00} + \langle Y_{20} (t = 0) \rangle Y_{20} (\theta)
\] (4.36)

with \( \langle Y_{KQ} (t = 0) \rangle = \sum_{J,J'} \frac{(-1)^{J'}}{\sqrt{4\pi}} \left( \begin{array}{c} 2J' + 1 \\ 2J + 1 \end{array} \right)^{1/2} \begin{pmatrix} J' & J \\ 0 & 0 \end{pmatrix} \langle T(J'J)_{KQ} (t = 0) \rangle \)

The \( Y_{KQ}(0,\phi)s \) are the spherical harmonics functions and the calculation result of \( I(0, t=0) \) gives an identical distribution as was obtained with the semiclassical treatment (for all \( J_0 > 0 \) in a \( \Sigma-\Sigma \) transition).

Propagation in time is accomplished by solving the Liouville equation for the excited density matrix, which in our simple case results in,

\[
\frac{\partial}{\partial t} \rho_{11} = \frac{\partial}{\partial t} \rho_{22} = 0
\]

\[
\rho_{12}(t) = \exp(-i(E_{J_0-1} - E_{J_0+1}) t) \rho_{12}
\]

\[
\rho_{21}(t) = \exp(+i(E_{J_0-1} - E_{J_0+1}) t) \rho_{21}
\] (4.37)

The diagonal terms stay constant, while the off-diagonal coherence terms evolves with the exponential of the energy difference between the two excited rotational levels.

The corresponding analytical expressions for \( <Y_{00}(t)> \) and \( <Y_{20}(t)> \) are,
\[
\langle Y_{00}(t) \rangle = \frac{1}{\sqrt{4\pi}}
\]
\[
\langle Y_{20}(t) \rangle = \frac{1}{\sqrt{20\pi(2J_0+1)}} \left\{ (J_0(J_0-1) + (J_0+1)(J_0+2)) + 6(J_0+1)J_0 \cos(\omega t) \right\}
\]

(4.38)

for the limit of \( J_0 \to \infty \), \( \langle Y_{20}(t) \rangle \) converges rapidly to,

\[
\langle Y_{20}(t) \rangle_{J_0,\to\infty} = \frac{1}{\sqrt{20\pi}} \left\{ \frac{1}{2} + \frac{3}{2} \cos(\omega t) \right\}
\]

(4.39)

which, together with \( \langle Y_{00}(t) \rangle \) gives the same time-dependent axial distribution, \( I(0, t) \), as was obtained from the semi-classical model.

Moving on to the final state distribution, after propagation of the intermediate state density matrix, the state-multipoles are calculated and rotation transformed to the probe E-field direction according to,

\[
\langle T(J', J) \rangle_{KQ}^{rot} = \sum_{q} \langle T(J', J) \rangle_{Kq} D(\theta_r)^{\ell^*}_{qQ}
\]

(4.40)

The rotated state multipoles may have \( Q \neq 0 \). Further, since the intermediate level have a larger \( J \) value in the state \( J_0+1 \) compared to the ground state \( J_0 \), the corresponding density matrix to the rotated state multipole, have terms with \( |M| > |M_0| \)!

This density matrix is now excited to the final state via a similar transition as eq 3. Same optical selection rules now populate the rotational states \( J_0-2, J_0 \) and \( J_0+2 \) in the final state. Different excitation paths to the same final \( J \) are added. The total population of the final state is proportional to the trace (\( \rho \)) (the sum of the diagonal elements \( \langle JM | \rho | JM \rangle \)), which simplifies analytical calculations to some extent, but the final expressions now becomes quite lengthy. I used Mathematica to calculate the final parallel and perpendicular signals. Analytically, in the limit of \( J \to \infty \), the final expression converges rapidly to the semi-classical results (less than 1% deviation already at \( J_0=5 \)). The beating terms, as in eq. (4.26), arise from excitation paths connecting the same initial and final rotational states, going via an intermediate state rotational coherence term, or roughly speaking, the paths have to meet at the end to interfere. In this case, due to the optical selection rules on \( J \), the only possible two paths ending at the same \( J \) are: \( J_0 \to J_0+1 \to J_0 \) and \( J_0 \to J_0-1 \to J_0 \), via the intermediate state coherence term \( \langle T(J_0+1, J_0-1) \rangle_{KQ}^{rot} \) after rotation, and give a signal of the form,

\[
S = C_1 + C_2 \cos(\Delta \omega t)
\]

(4.41)

Where the \( C \)'s are constants and \( \Delta \omega \) is the energy difference between the intermediate states \( J_0+1 \) and \( J_0-1 \). From the definition of the state multipoles, eq.(4.35), the coherence terms in the intermediate state, with different \( J' \) and \( J \), are necessarily
connected with $K = 2$. The rotation transformation tensor, $D(\theta_r)^{K-2*}_{00}$ of eq. (4.40) being relevant for calculation of the final state population, contains the factor $(3\cos^2 \theta_r - 1)$, which is zero for the magic angle, $\theta_r = 54.7^\circ$. Thus, all coherence terms $\langle T(J_0 + 1, J_0 - 1);_{\text{rot}} \rangle$ are zero at magic angle, and no beating of this kind exists in the final population. This is also valid for a multiple of intermediate, coupled states, as the pairs $\Lambda', \Lambda$ are treated separately and the rotation transformation tensor does not depend on $\Lambda$. Given the conditions a) linearly polarised pump and probe pulses (multipoles of $K=1$ absent) b) pump and probe in magic angle and c) isotropic detection proportional to final state population, the measured signal is free from rotational beating, no matter what electronic symmetries are involved. The only rotational properties remaining in such a magic angle measurement are 1) the centrifugal correction to the potential curves and 2) the rotational degeneracy $(2J_0+1)$ (P,Q,R branches not resolved) in the thermal averaging.

The conclusion of these quantum mechanical calculations is that the semi-classical model with the results presented above is satisfactory when $J_0 > 5$ and converges as $J_0 \to \infty$.  

5 Summary of the attached papers

I will introduce and summarize papers 2 and 3 in chapter 5.1, paper 1 in chapter 5.2 and paper 4 in chapter 5.3.

5.1 Vibrational quantum wavepacket dynamics in the Rb$_2$ A-state system

The strongly coupled A and b states of Rb$_2$ are well suited for real time wavepacket dynamic studies, the intermediate coupling strength giving strong non-adiabatic dynamics. For short delay times, advantage of the pump-probe technique over high-resolution c.w. spectroscopy can be expected, since the pump-probe technique eliminate molecular rotation dynamics (measured at magic angle of pump and probe polarisations). Further, the theoretical treatment of wavepacket propagation does not depend on individual energy eigenvalues in the strongly perturbed A-state system, but uses the potential curves with coupling elements as means of driving the wavepacket evolution.

To start with, I will describe in words our interpretation of the quantum wavepacket dynamics of a single molecule in this system.

Working in Hund’s case a [30] and using the diabatic potential curves (with respect to the spin-orbit coupling) of fig 1., the pump pulse creates a wavepacket on the inner limb of the A $^1\Sigma_u$ state. The spin selection rule, $\Delta S = 0$, together with Frank-Condon factors, prevent direct excitation of the b $^3\Pi_u$ state [30]. The excited wave-packet propagates outwards toward the crossing of the A $^1\Sigma_u$ and b $^3\Pi_u$ potential curves, coupled by spin-orbit coupling of intermediate strength, $V_{SO} = 70$ cm$^{-1}$. As the wavefunction transfer probability decreases with potential energy difference, transfer proceed mainly at the curve-crossing (+/-0.1 Å). The wavepacket splits into two pieces of about equal size, as it passes through the crossing. One remains on the A $^1\Sigma_u$ state and one is born on the b $^3\Pi_u$ state, both approaching the outer limbs of the potential curves. Thus, the system represents maximum non-adiabatic dynamics.

The probe pulse laser-molecule interaction creates an effective probe r-window on the b $^3\Pi_u$ state outer turning point, just to the right of the curve-crossing. Probing of the A $^1\Sigma_u$ state is prevented by the $\Delta S = 0$ selection rule, as the final state is a triplet state as well as the b state.

The propagation time for the original wavepacket, created at delay time zero (centre of the laser pump pulse), to deliver half of its size to the outer turning point of the b $^3\Pi_u$ state is about 300 fs. This gives the first peak of Fig 4 in paper 3.

Now, the future of the two nearly equal size wavepackets, one returning from the outer limb of the A-state, and one returning from the outer limb of the b-state, contain quite remarkable features.

Following one, say the b-state portion, it will split into two fragments (again of nearly equal size) on its inward passage through the curve-crossing, one remaining on the b-state and one is born on the A-state. Coincidently, these two fragments will return to the crossing, after bouncing back from the inner turning points of the potential curves,
at the same time. They overlap at the crossing, and will therefore interfere. As the amplitudes are nearly equal, full interference contrast is obtained. The situation is analogous to a pulsed optical Michelson interferometer, although here we have ‘matter waves’ instead of electromagnetic waves. Depending on the phase of the two interfering wavepacket fragments, constructive interference may put the combined wavepacket (wavefunction amplitude of twice the size of each interfering fragments) into solely the A-state or into solely the b-state. Changing rotation quantum number \( J_0 \), keeping ground state vibration quantum number \( v_0 \) fixed, creates a semi-continuous change of potential curve shapes and thereby a continuous change of the phase difference of the interfering wavepacket fragments. In the extremes of the interference \( (n \times \pi) \), the outgoing road chosen by the combined wavepacket, proceeding outwards from the curve-crossing, is scanned between the A-state and b-state as \( n \) increase with \( J_0 \). This oscillatory interference scan-behaviour is seen in fig 8 of paper 3. The trajectory of constructive interference back to the b-state is, by us, called bistable mesobatic trajectory, as the combined wavepacket will always return to the outer limb of the b-state. The trajectory of constructive interference to the A-state we call astable mesobatic trajectory, as the wavepacket will switch outgoing road every time the two fragments interfere on their outward passage through the crossing.

Similar oscillation between bistable and astable mesobatic trajectories exist if \( J_0 \) is kept constant while \( v_0 \) is increased, as the created wavepacket will reside at a higher energy position in the excited states, where the interference phase difference will be different. This oscillatory dynamics should be reflected in the relative positions of energy levels, and has been observed in higher levels of the \( \text{Rb}_2 \) A-state system, using high resolution continuous wave laser techniques [33]. Their analysis of high lying states is simplified by the fact that the molecule spends most of its time at large internuclear distances, remote from the crossing point. There, the S-O coupling value is nearly constant and equal to the dissociation limit. Also, ab initio calculation of potential curves, in the region of large internuclear distances, is simplified by neglecting core-core effects.

Returning to the original A-state wavepacket’s first passage through the crossing, we may instead follow the portion remaining on the A-state. As for the b-state portion, it will also split into two nearly equal fragments going inwards through the crossing, one remaining on the A state, and one created on the b-state. From this point, along the bouncing off at the inner potential walls, and back to the crossing, the dynamics is quite the same as described above for the b-state portion. Specifically, the condition of bistable and astable mesobatic trajectories are simultaneously fulfilled for both A- and b-state portions. When the A-state portion is in a bistable mesobatic trajectory, so is the b-state portion, and similar for the astable mesobatic mode. A fascinating revival phenomena occur for the astable mode after two vibration periods, where each original A-and b-state portions has interchanged its outgoing roads after their fragment interference. On returning to the curve crossing, going inwards, they have thus travelled the same ‘distance’, and will interfere constructively back to the A-state, creating an identical copy ( apart from a \( \pi \) phase shift) of the originally pumped A-state wavepacket. Hence, thanks to the intermediate coupling strength and perfect timing for interference, an ultra-short revival time of only 1.5 ps occur. We do not directly see this full revival in the pump-probe scheme taken, since the probe position is not at the inner turning point of the A-state.
Taking the thermal average over $v_0: 0 \rightarrow 15$ and $J_0: 0 \rightarrow 300$, one might expect that most of the interference is washed out [11]. As shown in paper 3 & 4, experimentally and theoretically, this is not the case. The interference shows its fingerprint and even scanning is possible for a hot sample. Taking the Fourier transform of the thermally averaged pump-probe time traces, the peaks correspond to the bistable and astable mesobatic trajectories. As the interference follow a sinusoidal pattern, more bistable and astable mesobatic trajectories occur than in-between trajectories. In addition, the phases of fig 8 in paper 3 vary less at the mesobatic bistable and astable extremas than in-between traces. Further, since the thermal distribution peaks around $J_0 = 120$, certain scanning possibility still exist, by changing the laser pump wavelength. This is also verified in experiments as well as in simulations. The scanning result in a change of relative amounts of bistable and astable mesobatic contribution. The ’phase’ of the scanning (relative amounts of bistable and astable for a certain pump wavelength) is however too sensitive (due to interference) to e.g. the potential curve shapes to be matched between the simulations and the experiments.

Recalling the discussion on autocorrelation, experimentally, one would obtain the autocorrelation, $b(t)$ if the probe point is identical to the originally created wavepacket, namely on the inner turning point of the A-state. This is not our case, where we probe the outer turning point of the b state. So the frequencies obtained by Fourier transforming our probe signal is not the wavepacket’s frequency contents, but only contains the frequencies that our probe pulse can detect. Further, the final state, to which we probe the intermediate wavepacket, may also influence (e.g. via the probe point) the FFT (Fast Fourier Transform) spectrum of our experimental signal. However, our experimental signal can be simulated theoretically and serves as an indicator of the correctness of the simulation. As an example, for the bistable trajectory, the signal would be the same if the b state was dissociative to the right of the crossing instead of bound. By including thermal averaging, the signal probe different types of dynamics, and the experimental indicator becomes a stronger judge of the simulation quality.

By having the probe point at the outer turning point of the b-state, the signal and its frequencies are simplified compared to probing the inner turning point of the A-state. For instance, the bistable trajectories show up as a single frequency on the outer limb of b, while both bistable trajectories give signals at the inner limb of A.

To summarize, the highlights of papers 2 & 3 are the characterisation (e.g. the characteristic frequencies in the Fourier transform of their time-traces) of the mesobatic trajectories, and, in a thermal average (T= 700 K), that they are both visible and that their relative amounts are changeable by scanning the pump wavelength. Both experimental results and theoretical simulations support these conclusions. However, the experiments and simulations deviate in the ‘phase’ of mesobatic contributions for a specific pump wavelength. This is not surprising, as the interferometric dynamics is highly sensitive to input parameters, and such high accuracy on the theoretical side is not available.

An obvious question that arise after this discussion, is if the spectrum of the experimentally measured time-trace is unique for the interference conditions as described above. In other words, how does the spectrum of thermally averaged time-traces look like if the interference conditions are not met. Although a full analysis of
this issue has not yet been done, the following test do support the unique connection between the obtained spectrum and the occurrence of mesobatic trajectories: Bring back the harmonic potential substitution of the A-and b-states respectively, one can manipulate the potential curves in a more controlled fashion. To start with, the harmonic potentials are adjusted to fulfill the interference timing condition, that both fragments return to the crossing at the same time, as is the believed case of the Rb$_2$ molecule. Curve-crossing point, excitation and probe positions, and coupling strength are similar to the real A-and b-potentials. The normalised spectra of the time-traces are plotted in Fig 5.1 a) as a function of $J_0$ for a given $v_0 = 3$, analogous to fig 8 of paper 3. We recognise, again, the characteristic oscillatory pattern, switching between bistable and astable mesobatic trajectories with increasing $J_0$. The frequency values, pattern ‘phase’ and period, etc, are a bit different to the real Rb$_2$ case, due to the approximate harmonic potentials. Now, decreasing the b-state force-constant, keeping the curve-crossing point fixed, the returning b-state wavepacket fragment, after making the left-hand roundtrip (with respect to the crossing point), arrives just after the A-state fragment to the crossing. Thus they do not overlap, cannot interfere, and the timing condition of interference, as described above, fails. The resultant spectrum is shown in Fig 5.1 b).

![Fig 5.1](image)

Fig 5.1 Contour diagram of the frequency contents of the time traces versus $J_0$ for the a) ‘on’ mesobatic interference condition and b) ‘off’ mesobatic condition (by stretching the harmonic b-state potential ). $\lambda_{\text{pump}} = 910$ nm.

The oscillatory pattern is lost, and the frequencies look quite random with increasing $J_0$. Also, averaging over $J_0$ for a single $v_0 = 3$ gives a single peak at 49 cm$^{-1}$ in contrast to the Rb$_2$ case where the bistable trajectory give a single peak at 56 cm$^{-1}$, and the astable trajectory give peaks at 25, 49 and 72 cm$^{-1}$. The higher frequencies, above 49 cm$^{-1}$, of fig 1.b) average out to zero as the phases of the complex frequencies become increasingly random with $J_0$ for larger frequencies. Thus, it seems that the interference spectrum is unique, but further investigation of the thermal averaging is required to prove this conclusion.
5.2 Vibrational quantum wavepacket dynamics in the Rb\textsubscript{2} D-state system

With reference to fig 2.1b) in chapter 2, the first experiment on the D-state system set out to excite a wavepacket on the D \textsuperscript{1}Π\textsubscript{u} state and probe the predissociated atoms arriving at the atomic state 4D.

5.2.1 Predissociation to the Rb 4D atomic state

The pump was set at 428 nm, exciting a wavepacket on the D state, energetically just above the atomic 4D level. The probe is set to 954 nm, in resonance with atomic transition 4D → 8P. Detection is fluorescence 8P → 5S in the Rb atom using a UG 11 colour filter, thus also detecting the cascading 7P → 5S transition. The long time-trace is shown in Fig 5.2.

\begin{align*}
\text{fit: } y &= C_2 - C_2 \exp\left(-t / \tau \right) \\
\tau &= 90 \text{ ps}
\end{align*}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{Fig_5.2}
\caption{Pump probe trace of the excited Rb\textsubscript{2} D state and probed atomic 4D dissociation products.}
\end{figure}

In contrast to the discussion by Zhang et al [15] and Breford et al [14], our results indicate that the atomic 4D products have a very slow rise time of around 90 ps. However, in accordance with Zhang et al, we also propose that the state involved in the predissociation of the D state to 4D atomic level, is the \( (1) \text{ } \Sigma^+_u \) state, see fig 3.3.8, interacting via spin-orbit coupling.

Unexpectedly, at short delay time (\( \Delta t < 10 \text{ ps} \)), the pump probe time trace oscillate, which can only be explained as originating from molecular dynamics. We propose that the atomic 4D – 8P is not the only probe channel at 954nm, but also the \( (3) \text{ } \Sigma_u \) shelf state and \( (4) \text{ } \Sigma_u \) states (see later on) are probed to Rydberg states. The signal in fig 3.3.5 is therefore an overlap of molecular and atomic products. To isolate the molecular probe channel, the probe wavelength was tuned off atomic resonance to 927 nm, which is the probe wavelength used in the rest of this chapter and in paper 1.
5.2.2 Probing off atomic resonance at 927nm

\( \lambda_{\text{pump}} \) is kept at 428, \( \lambda_{\text{probe}} \) is set to 927nm and fluorescence is detected from atomic 8P to atomic groundstate 5S at 335 nm. The experimental pump-probe trace shown in Fig 5.3 is detected with a UG 11 (transmitting 335 nm) colour filter. Pump and probe polarisation directions are set to magic angle.

![Pump-probe trace of the D-state systems, using \( \lambda_{\text{pump}} \) = 428 and \( \lambda_{\text{probe}} \) = 927nm.](image)

The time zero is calibrated using acetone gas, see Fig 3.3 and chapter 3. The pump-probe signal levels out at about 200 counts /s, after 20 ps and stays at that constant level for longer delay times.

Interpreting the experimental results, we put forward the following model:

Two wavepackets are launched from the ground state (\( r_e = 4.2 \ \text{Å} \)), one to the \((3)^1\Sigma_u \) shelf state, and another simultaneously to the \( D^1\Pi_u \) state [3]. The D state channel wavepacket is 10 times more intense than the shelf state channel wavepacket (due to Franck-Condon factors). Both have \( r_e = 4.2 \ \text{Å} \) and a width of 0.1 Å (corresponding energy width of about 120 cm\(^{-1}\)), and their dynamics will proceed essentially independently. The dynamics of the shelf state consist of oscillations in a single potential (of unusual shape though) and can be classified as adiabatic. On the contrary, the dynamics of the D state include potential curve-crossings that couple out part of the D state wave function, and may be classified as non-adiabatic.

Both channels will be probed (927 nm) to dissociating Rydberg states, ending up in the same 8P atomic state. Hence the signal seen in Fig 5.3 is composed of both these two channels. The D state system is responsible for the peaks at 1.0 and 2.1 ps time delay, while the shelf state contributes with large peaks at 3.5, 8.5 ps etc with a 4.8 ps period. On the negative side of delay time zero, the 927 nm beam pump the \( A^1\Sigma_u \) state, while 428 nm beam probe the inner turning point of \( b^3\Pi_u \) which couple to the A state via the spin-orbit coupling \( V_{\text{SO}} = 70 \ \text{cm}^{-1} \). This is precisely the A-state.
system studied in papers 2, 3 and 4, but probe transition is different due to the different ‘probe’ wavelength (here \( \lambda_{\text{probe}} = 428 \text{ nm} \), in papers 2,3 and 4 \( \lambda_{\text{probe}} = 1700 \text{ nm} \)).

(3)\(^1\Sigma_u^+\) shelf state channel:

The wavepacket’s semi-classical behaviour, within one potential curve (Fig 5.4 a)), makes it possible to approximately simulate its classical trajectory by the classical equations of motion, as a starting point in the analysis,

\[
\frac{\partial r}{\partial t} = \frac{p}{m} \quad \frac{\partial^2 r}{\partial t^2} = -\frac{1}{m} \frac{\partial V}{\partial r} \quad r(0) = 4.2 \quad \frac{\partial r}{\partial t} (0) = 0 \quad (5.1)
\]

This system of differential equations may be solved with the Runge Kutta algorithm [34]. At \( t = 0 \), the wavepacket is created on the left hand side at \( r = 4.2 \text{ Å} \), having zero momentum. The classical trajectory shows that the wavepacket spends most of its time in the shelf region, where kinetic energy is low. If a larger \( r(0) \) value is chosen, the wavepacket has lower energy, and the classical trajectory is a harmonic oscillation in the lower part of the potential well.

![Fig 5.4 Classical trajectories in the (3)\(^3\Sigma_u^-\) state.](image)

In the experiment published in paper I, the wavepacket is created just above the shelf energy level.

A few snapshots of quantum wavepacket propagation in the (3)\(^1\Sigma_u^+\) shelf state is shown in Fig 5.5.
Fig 5.5 Wavepacket propagation in $(3)^1 \Sigma_u$ shelf state. Snapshots at $t = 0$ ps; $t = 0.5$ ps; $t = 3.8$ ps; $t = 5$ ps. $|\Psi|^2$ is plotted against $r$ where $3.5 < r < 14.0$ Å.

The probing of the wavepacket can either be implemented by adding a time dependent coupling up to a final state’s potential curve, or, in a more crude way, putting an $r$-window where the wavefunction is probed. The signal is then proportional to the integral of $|\Psi|^2$, over the window region. No thermal averaging has been performed on the D-state system so far.

Fig 5.6 Potential curves of Rb$_2$ D and Shelf state. The dotted line illustrate the ion-ion bonding potential, responsible for the shelf shape, through a series of complicated avoided crossings. The shaded region show the probe window.
The probe pulse is energetically in resonance with a proposed Rydberg state just at the classical outer turning point (11 Å < r < 12 Å). The Rydberg state dissociates out to the 8P atomic level. The scheme is sketched in Fig 5.6. The shelf state is shown together with the D state. The two states do cross, but due to symmetry reasons, they can only couple via the ‘L uncoupling element’, which is estimated to be less than 3 cm\(^{-1}\) at \(J = 100\) [24]. The influence of this coupling is small and is neglected in the simulations.

The wavepacket makes classical oscillations back and forth, just above the shelf barrier. Simulation of the signal is shown in paper 1, Fig 4. Due to the shelf shape, the signal is zero until 1.7 ps delay, and has an oscillation period of about 4.8 ps.

D\(^1\Pi_u\) state system channel:

Three states are used to simulate the results. The D state is spin-orbit coupled to both the \(^3\Sigma_u^+\) state and to the \(^3\Delta_u\) state. The \(^3\Sigma_u^+\) and \(^3\Delta_u\) are not coupled directly (no crossing between these two states). Coupling strength is set to 20 cm\(^{-1}\) to both states, which is the ‘pure precession’ upper limit estimation [24].

![Fig 5.7 D-state system.](image)

Fig 5.7 shows the potential curves together schematic wavepackets numbered from left: 1. \(t = 0\) fs: starting wavepacket (on D state, \(r_e = 4.2\) Å). 2. \(t = 450\) fs: remaining D state wavepacket (after half a D state period). 3. \(t = 550\) fs: portion of D state wavepacket coupled over to the \(^3\Sigma_u^+\) state at the crossing at \(r_e = 5.1\) Å. 4. \(t = 650\) fs: portion of D state wavepacket coupled over to the \(^1\Delta_u\) state at the crossing at \(r_e = 4.7\) Å. This wavepacket dissociates into 4D\(^3/2\) + 5S atoms.

The split operator Fourier transform method is relying on that the r-grid is covering the whole wavefunction, which fails when the wavefunction on the \(^3\Delta_u\) state reaches...
the right-side limit. This results in large distortions of the wavefunction. To avoid this problem, a negative complex part is added to the $^3\Delta_u$ potential curve on the right hand side, 12 Å < r < 20Å [44]. The result is a negative exponential part in the time propagator, which damps the amplitude of the part of the wavefunction that enters this zone. A compromise between reflection and non-complete damping has to be made. In my simulation, the remaining wavefunction, after the damping, gives a completely neglectable distortion to the overall dynamics.

Probing point is at the right-hand side classical turningpoint (7.0 Å < r < 7.2 Å) of the $^3\Sigma_u^-$ state, up to a proposed triplet Rydberg state. The $^3\Delta_u$ state depletes the D state population (finally ending up at atomic 4D), each time the D state wavepacket reaches the left side of the potential. Thus, during the first oscillation in the D state, the wavepacket will couple over to the $^3\Sigma_u^-$ state twice, on the way out and then on the way in. This gives the two signal peaks, at 1.0 and 2.1 ps time delay in Fig 5.3. Thereafter the signal from $^3\Sigma_u^-$ is exponentially decayed due to the loss of wavefunction through the $^3\Delta_u$ route. Simulation signal is shown in paper 1, fig 4.

Scaling the D state system with a factor 10 over the shelf state signal (the transition probabilities are unknown), and adding the signals result in the final ab initio simulation of the wavepacket dynamics, shown in paper 1, fig 3b.

### 5.2.3 Simulating the D state decay

In order to compare our simulations with the earlier experiments by Zhang et al. [15], we put the probe window on the D state, close to the outer turning point, with the result shown in Fig 5.8.

![Fig 5.8 Probing the D state.](image)

For short wavelengths, the decay is around 5 ps, and for longer wavelengths the decay is around 1 ps. The reason for this effect is that the less energetic wave packet travels slower across the crossing, and couples stronger, in the sense of the Landau-Zener model [16]. The oscillation is the D state vibration. The splitting is due to the
probe-window being slightly inside the outer turning point. These features agrees with the results of Zhang et al. Discrepancies are the depth of the signal dips and a constant signal background. Including rotational averaging, decreasing coupling strength to $^3\Delta_a$ (the high value of 20 cm$^{-1}$ was chosen to damp the peaky signal at long delays, an effect thermal averaging would do instead), and including more states are suggested improvements in the modelling, which will be investigated in the near future. A lower S-O coupling strength, around 5 cm$^{-1}$ between the D$_1\Pi_a$ and the $^3\Delta_a$ state would directly explain the slow rise of the atomic predissociated population at 4D as shown in fig 5.2.

5.3 Rotational quantum wavepacket dynamics on the Rb$_2$ A-state system

The anisotropy was measured experimentally (pump 910nm, probe 1700 nm) by averaging alternatively parallel and perpendicular laser polarisation signals, and then inserted into eq. (4.27). A large number of scans were done to receive high signal to noise ratio. The obtained anisotropy resembles a simple $\Sigma-\Sigma$ transitions, but with a small oscillation structure, well above the noise level and reproducible. We propose they are due to the J-dependence of the isotropic magic angle signal. The limiting values are slightly less than 0.4 and 0.1, which we think can be due to a small deviation from pure Hund’s case a towards Hund’s case c. Thus, the probe transition could have a $\Delta\Omega = 1$ contribution as well as $\Delta\Omega = 0$, for the $\Pi-\Pi$ probe excitation. This means that we may have some perpendicular contribution to the parallel probe transition. A parallel-perpendicular sequence has a negative thermally averaged anisotropy, and would thus reduce the overall anisotropy.

5.3.1 Argumentation for approximately isotropic detection

In general, the final state molecules have a non-isotropic distribution, as the laser-molecule interaction is non-isotropic. Detecting the fluorescence in a certain direction, may lead to an over-or underestimate of the signal compared to isotropic detection (proportional to final state population) [42]. The following discussion is meant to support the approximation used in this thesis that detection is isotropic in our specific cases. Firstly, the fluorescence detection arrangement was designed to optimise photon collection efficiency, covering roughly 1/6 of the $4\pi$ solid angle. This makes detection more isotropic than for a uni-directional detection case.

Rb$_2$ A state system:

The detected fluorescence is the dissociated Rb atomic transition, 5P$_{3/2}$ to 5S$_{1/2}$. The fluorescence is time-integrated over a few atomic 5P$_{3/2}$ lifetimes ($\tau \approx 30$ ns). As both fine structure (S-O coupling, J=L+S) and hyperfine structure (F=J+I, I=5/2) has a shorter oscillation time scale than 30 ns (about 10 ns for hyperfine structure), these couplings will diminish an original alignment of the dissociated 5P$_{3/2}$ atoms. For atoms, the total angular momentum vector F remains constant in time, while J and I make precession around F. As the spin-orbit interaction couples stronger than the hyperfine interaction, J remains a good quantum number, and L and S make precession around J. In total, the orientation of the L vectors of the 5P$_{3/2}$ atoms, being relevant for the fluorescence electric fields orientations, will spread out due to its
precession motions about F and J. Integrating the signal in time thus leads to a more isotropic L vector orientation, compared to a case without these interactions.

The molecular dissociation is probably not instantaneous. The shallow final state, dissociates the molecules during a timescale of more than a picosecond, during which the molecule has time to rotate over a certain angle, and this may leads to a smearing out of dissociated atomic orientation.

In estimating a ‘worse case’ upper deviation from isotropic detection, the semi-classical distributions of the final state axis distribution (Σ-Σ-Σ) may be used together with instant dissociation approximation and ignoring fine and hyperfine interactions. Exchanging the final state to a molecular Π state which then dissociates into one 5S and one 5P atom, the 5P atom having its angular momentum projection, \( M_L = 1 \), along the dissociated molecular axis. Projecting out the resulting atomic fluorescence in a direction perpendicular to the laser beam, results in an anisotropy signal (for a single J) oscillating between about 0.3 and −0.15, instead of the isotropic detection range 0.4 and −0.2. Including spin-orbit fine interaction, the anisotropy is slightly larger than isotropic detection.

Rb\(_2\) D state system:

As for the A state system, the main argument for isotropic detection approximation, is the fine and hyperfine interactions swirling around the L vectors of the final dissociated excited Rb P atoms, being the upper level in the atomic fluorescence to ground state. The decrease of orientation comes from time integration of this atomic fluorescence over a few lifetimes (\( \tau > 200 \) ns for Rb 8P). Rotational smoothing during dissociation, and large fluorescence capture angle also helps out, but since the final states are unknown, the dissociation time is hard to estimate.

### 5.3.2 Simulating the anisotropy time trace

A few assumptions are made:

- As argued above, the detection signal is assumed proportional to the final state population.
- Using Hund’s case a) electronic symmetries, the probe transition is a parallel \(^3\Pi_0 - ^3\Pi_0\), which in the high J limit equals a \( \Sigma - \Sigma \) transition. The rotational Q branch is in the \(^3\Pi_0 - ^3\Pi_0\) transition forbidden as it is for a \( \Sigma - \Sigma \) transition, and the deviation of 3J symbol values for \( \Lambda = 0 \) (\( \Sigma \)) or \( \Lambda = 1 \) (\( \Pi \)), is approaching zero rapidly with J.
- The spin-orbit coupling of the intermediate A \(^1\Sigma\) and b\(^3\Pi\), is isotropic (couples all M equally with \( \Delta M = 0 \)) and have the selection rule \( \Delta \Omega = 0 \) and \( \Delta J_{tot} = 0 \), and \( \Omega = 0 \) for the A \(^1\Sigma\) state. Thus, in the process of jumping over from the singlet to the triplet state, the increase in the electronic L projection on the molecular axis is cancelled by the increased S projection, keeping \( \Omega = 0 \).

With these approximations, valid in the semi-classical high J limit, we have reduced the rotational transitions to a simple \( \Sigma - \Sigma - \Sigma \) case, and as shown by the q-m calculations
we may even use our simple semi-classical formulas derived in chapter 4.3.1. In the magic angle measurements, for the vibrational dynamics, the influence of rotation on the electronic-vibrational dynamics was limited to the centrifugal potential term and a degeneracy factor for the thermal average. For a single molecule, we will always assume that it’s rotation motion is decoupled from it’s electronic-vibration motion. Is the rotation affected by vibration?

Classically, when a rotor vibrate, it’s angular velocity changes as the moment of inertia changes in time. In the molecular case, the angular velocity, eq. (4.24), depends on \( \langle 1/(R(t))^2 \rangle \) via \( B_e \), where \( \langle 1/(R(t))^2 \rangle \) is the expectation value of the square of the reciprocal of the internuclear distance, \( R(t) \) \[43\]. \( \langle R(t) \rangle \) for a typical magic angle time trace is shown in Fig. 5.9.

\[
\langle R(t) \rangle (\text{Å})
\]

\[
0 \quad 2 \quad 4 \quad 6 \quad 8 \quad 10 \quad \text{time (ps)}
\]

Fig 5.9 Calculated \( \langle R(t) \rangle \) from a typical magic angle wavepacket simulation of the coupled A and b states in the Rb\(_2\) A-state system.

Modelling a ‘worst case’ influence of the varying \( B_e \) value on the anisotropy, \( R_A \), a harmonic potential was used with \( \langle R(t) \rangle \) oscillating between the maximum and minimum of Fig 5.9. As seen in Fig 5.10, the resultant anisotropy of a single J is almost identical to a result with constant \( B_e \) value.

\[
R_A(t)
\]

\[
0 \quad 100 \quad 200 \quad 300 \quad 400 \quad 500 \quad \text{t(ps)}
\]

Fig 5.10 Vibrational influence on rotation anisotropy for a single J. The fast oscillation is almost invisible.
The equilibrium value of $B_e$ chosen, does influence the oscillation structure in the average anisotropy, since the period for a given $J$ change. The conclusion is that vibration has small effect on rotation for our case, and we may choose a fixed, average, internuclear distance for the $B_e$ value of the semi-classical expressions.

In the following section, I will use formulas referring to Zewail et al. [41], valid for a $\Sigma-\Sigma-\Sigma$ transition. The signal from a single molecule can thus generally be written in the form (the vibration is not stated explicitly, but is included in $P$ and $A$),

$$I(J, t, \theta_r) = P(J) \cdot A(J,t) \cdot \{P_0 + C(\theta_r) \cdot P_2(J, t)\}$$  \hspace{1cm} (5.2)$$

Where $J$ is now the ground state rotational quantum number, $P(J)$ is the thermal weight, $A(J,t)$ is now an isotropic time-and rotation dependent scalar (the magic angle electronic-vibrational dynamics signal) and the $\{\}$ term is a purely geometric term (due to rotation). That is, the electronic-vibrational and rotational contributions factorize. The geometrical term $\{\}$ consists of one isotropic part, $P_0 = 1$, which is the zero-order Legendre polynomial and also the $K = 0$ state multipole of the intermediate state. The second part of $\{\}$ is a non-isotropic alignment term, $P_2(\cos(\eta(J,t))) = (3(\cos(\eta(J,t))^2)-1)/2$, the second-order Legendre polynomial and also the $K = 2$ state multipole, scaled by the pump-probe E-field geometry dependent factor $C(\theta_r) \propto P_2(\cos(\theta_r))$

The important part of eq. (5.2) is that the $A(J,t)$ factor is strongly dependent on $J$ for our A-state system, where, due to the interference, the bistable and astable trajectories e.g. have completely different time-traces.

To start with, we see that the magic-angle signal is all-isotropic, since $C(\theta_r)$ is zero at $\theta_r = 54.7^\circ$. One can also show from eq. (5.2) [41] that,

$$I(54.7^\circ) = 1/3 \cdot (I(0^\circ)+2 \cdot I(90^\circ)) = P(J) \cdot A(J,t).$$  \hspace{1cm} (5.3)$$

Thermal average is simply obtained by summing eq. (5.3) over $J$.

Now, calculating the anisotropy of a single rotation state, $J$, by inserting eq.(5.2) into eq. (4.27) (the signals, $S$, of eq. 4.27 are here labeled $I$) one gets [41],

$$R_A(J,t) = 0.4P_2(\cos(\eta(J,t)))$$  \hspace{1cm} (5.4)$$

Which is equivalent to eq. (4.28). The anisotropy gives the pure geometric alignment, free from isotropic contribution.

Calculating the thermal average of the anisotropy, which is what we measure experimentally, the parallel and perpendicular signals, eq. (5.2) are averaged first, and thereafter inserted in eq.(4.27). Due to the $J$-dependence of $A(J,t)$, they do not cancel out in the thermal average, but rather weight the state-resolved anisotropies (anisotropy of a single $J$, $R_A(J,t)$) in a form,
\[
R_{A,\text{tot}}(t) = \frac{\sum_{j} P(J) A(J,t) R_{A}(J,t)}{\sum_{j} P(J) A(J,t)} \tag{5.5}
\]

Therefore, the statistical thermal average of the anisotropy is a sum of pure alignment terms, \(0.4P_{2}(\cos(\eta(J,t)))\), weighted by thermal population and magic angle, isotropic, electronic-vibrational dynamics, as was introduced in chapter 4.2. At a certain delay time, \(\tau\), the molecules having a large vibrational magic angle signal contribute more to the averaged anisotropy, then molecules with low vibrational signal.

If \(A(J,t)\) is not dependent on \(J\), it factors out in eq. (5.5) and cancels, and the averaged anisotropy becomes the smooth curve of Fig. 4.7. In our Rb\(_{2}\) A-state system case, however, \(A(J,t)\) is strongly J-dependent, and gives rise to the oscillation structure superimposed on the smooth curve. Inserting the magic angle simulations (used in papers 2 and 3) into (5.5), using \(R_{A}(J,t)\) for the semi-classical \(\Sigma-\Sigma-\Sigma\) case as described above, and Boltzmann factors for \(P(J)\), we get the simulation result shown in paper 4.

The simulation has similar oscillation structure as the experiment, but the positions of the peaks do not match. However, as was argued in papers 2 and 3, the sensitivity of the trajectories on e.g. potential shapes, are to high for available ab-initio calculated potential curves. Thus, we do not know if a molecule in a certain ground state \((J,v)\) will perform bistable, astable or in-between mesobatic trajectories, and this will of course influence at which time delays, \(\tau\), it contributes to the anisotropy.
6 Future perspectives

A few new angles to study the non-adiabatic curve-crossing wavepacket dynamics:

For the wavepacket, a) the probe-point may be changed by changing probe wavelength. Piles of this type of experimental data on the D-state system is awaiting to be analysed. For the A-state system, apart from scanning the probe point, it would be interesting to probe the A state to the right of the crossing, to see the ‘complementary’ signal to the one obtained in the current experiment. Or probing the inner limb of the A-state, where the full revival occur for the bistable mesobatic trajectory. b) The dynamics could also be studied by actively changing the shape of the pumped wavepacket, a field called quantum control. The easiest manipulation to play with is the laser pulse chirp, the time shift of the pulse-containing frequencies. The numerical simulation program is already prepared for chirped laser pulses. c) The anisotropy measurements on the A-state system was performed with fixed pump (910 nm) and probe (1700 nm) wavelengths. Scanning these should also affect the interferometric origin of the small oscillatory structure seen superimposed on the smooth transient anisotropy.

For the molecular parameters, potential curves and couplings may be perturbed by building clusters of Rb$_2$X$_N$, where X is some nobel gas atom, which would slightly change the Rb$_2$ wave function.

Cooling of Rb$_2$: Regardless of the failing performance of the 1st crossed beam apparatus, success in cooling Rb$_2$ would give a simpler, cleaner signal, which would complement the hot experiments done so far. At least, the numerical simulation load would greatly decrease with less vibrational and rotational levels populated in the ground state.

As briefly mentioned, mounting an ion detector, preferably with energy resolved electron detector, would give much higher sensitivity, as the ions can effectively be extracted and it’s background noise being very small. Different probe paths could be taken, and would give complementary information to the fluorescence detection. A technical issue is how to keep the detector clean from alkali Rb waist.

On the numerical analysis side, knocking on the door, is the inclusion of full probe pulse propagation instead of the use of the approximate, frozen wavepacket Rozen-Zener model, used so far. The validity of the R-Z model in our specific case would be tested, which is somewhat questionable in the Rb$_2$ A-state system, although we do get satisfying agreement with experiment. During the probe time of 120 fs, the wavepacket will definitely not stay still. The price to pay for probe propagation is cpu-time. Using R-Z model, the full time propagation needs only be done once. Since a propagating probe pulse would interrupt the intermediate state wavepacket, the probe time-propagation needs to be recalculated for every delay time, $\tau$.

Proving the uniqueness of the interference signatures of the experimental results of papers 3 to 5, e.g. by theoretically manipulate potential curve shapes, would extend our conclusions to include the other direction, that the experiment is a proof of existing mesobatic trajectories.
Applying the numerical simulation program to the D-state system would greatly improve the analysis. All potential curves (although the final ones are unknown) relevant may be inserted, pump and probe laser pulses time propagated, and thermal averaging performed.

A technical suggestion of experimental improvement is to avoid skimmer holes for the Rb$_2$ beam to be too cold, as the hole quickly jams up with solid Rb waist. Instead, a thermally isolated cooled capture cup for the Rubidium beam on the other side of the laser-molecule interaction should be mounted. Since the oven is loaded with 2g of Rb metal, which lasts a few days, quite a bit of Rb material is released from the oven, part of which is condensed on the fluorescence collection lens. A cooled capture cup would make the Rb material condense there instead.
7 Appendix

Spin-orbit adiabatic correlation limits using group theory:

A set of molecular states correlate adiabatically to either the upper or lower spin-orbit split 5P states. Group theory is a quick way to determine which atomic level, a molecular potential curve dissociate into. The following example determine the correlation limit for the \((1)^3 \Pi_g\) state, the final level of the A state experiment. All gerade molecular potential curves [3] correlating to 5P + 5S atomic state are shown in fig 4.1.

![Gerade potential curves correlating to 5P + 5S.](image)

Fig 4.1 Gerade potential curves correlating to 5P + 5S.

The Rb\(_2\) molecule belongs to the D\(_{\infty h}\) point group.

Step 1 :
The molecular states are decomposed into spin-orbit symmetries:
Using the direct product tables and species of spin functions tables [35], one get the following symmetries:

\( ^3 \Sigma_g^+ \) state:
\[ S=1 \Rightarrow \{ \Sigma_g^- + \Pi_g \} \]
\[ \Sigma_g^- \otimes \Sigma_g = \Sigma_g^- \quad \text{and} \quad \Pi_g \otimes \Sigma_g = \Pi_g \]

Likewise the other states give the symmetries :
\( ^1 \Pi_g \) :
\( \Pi_g \)
\( ^1 \Sigma_g \) :
\( \Sigma_g^+ \)
\( ^3 \Pi_g \) :
\( \Pi_g, \Sigma_g^+, \Sigma_g^-, \Delta_g \)
Step 2:
Resolution of species of atoms into the $D_{\infty h}$ symmetry:

5S atom:
- $S_g : \Sigma_g^+$
- $S = \frac{1}{2} : E_{1/2 g}$
- $\Rightarrow E_{1/2 g} \otimes \Sigma_g^+ = E_{1/2 g}$

5P atom:
- $P_g : \Sigma_g^- : \Pi_g$
- $S = 1/2 : E_{1/2 g}$
- $\Rightarrow E_{1/2 g} \otimes \Sigma_g^- = E_{1/2 g}$
- $\Rightarrow E_{1/2 g} \otimes \Pi_g = E_{1/2 g} ; E_{3/2 g}$

$5P_{1/2} + 5S : E_{1/2 g} \otimes E_{1/2 g} = \Sigma_g^+ , \Sigma_g^- , \Pi_g$

$5P_{3/2} + 5S : E_{1/2 g} \otimes E_{1/2 g} = \Sigma_g^+ , \Sigma_g^- , \Pi_g$
- $E_{1/2 g} \otimes E_{3/2 g} = \Pi_g , \Delta_g$

The correlation diagram is drawn in fig 4.2. The order of the molecular states is the order at the bound molecule, $r \approx 4.2 \text{ Å}$. States with the same symmetry do not cross.

![Correlation diagram](image)

Fig 4.2 Correlation diagram

Specifically, the $^3\Pi_g$ state correlates only to the $5P_{3/2} + 5S$ atomic state.
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