ATOMIC SCALE DYNAMICS OF THE CHEMICAL BOND

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Abstract

When a chemical bond is broken in a dissociation reaction, the process is so rapid that its temporal evolution cannot be observed by direct measurements. In this seminar, I give a theoretical description of the molecular dissociation dynamics and introduce a technique for recording real-time snapshots of the dissociation process with subangstrom resolution. In the end, I present an experiment that investigated the dissociation dynamics of NaI.
1 Introduction

One of the first human activities in the history of our civilization was recording of the order, duration and periodicity of the natural events. The development of calendars and clocks allowed humans to predict seasonal changes like floods and droughts which was crucial for their survival. Since then, the methods for measuring time were improving and the measurement of time and duration of events became an important concept in many areas of science.

Even though systematic recordings of the duration of the events can be traced back to the dawn of written language, until the 1800’s humans ability to perceive and record time was limited to the time sensitivity of our eyes and ears. The reaction time of the eye is around 0.1 second and the response of the ear is a thousand times faster than the eye, around 1 ms, the time interval in which we were able to perceive nature. In the nineteenth century, there was a major improvement of the technology and that enabled the development of new devices for resolving time intervals into subsecond domain that could capture changes in time imperceivable to the human senses.

One of the first recordings of time-resolved motion was the motion picture of a galloping horse recorded by Eadweard Maybridge in 1872 with the use of snapshot photography. He investigated if a galloping horse, at some point in its stride, lifts all four hooves off the ground simultaneously. For that purpose he developed a camera with a shutter that remained open for only two-thousands of a second. He used a line of 12 or 24 cameras along a track, with their shutters triggered by the horses legs breaking equally spaced trip-wires\[^1\]. Since then, variety of techniques were developed for recording events imperceivable to the human eye, like chronophotography, snapshot photography and stroboscopy with time resolving power of the order of microsecond. A major step forward in improving the time resolution was made with the discovery of lasers in 1960.

Shortly after the realization of the first ruby laser in 1960 by Maiman which emitted continuous EM radiation, new techniques were developed for generation of short pulses of EM waves. The use of techniques like Q-switching and mode locking enabled fast development of pulsed lasers and time duration of the pulses in the orders of picoseconds. In 1974 subpicosecond pulses from dye lasers were obtained by Chuck Shank and Eric Ippen at Bell Labs. The existence of such lasers opened the possibility for developing new methods for observation of events on the femtosecond time scale - the realm of molecular motion.\[^1\]

2 Molecular dynamics

Molecular motion is a dynamic process in which the atoms change their spatial configuration with time. When the atomic nuclei change their orientation relative to the center of mass of the molecule, the motion is characterized as rotation. Molecular vibration is a motion in which the internuclear distance between the atoms changes periodically. Additionally, there can be transition of the electrons between different molecular orbitals which under certain conditions can trigger nuclear motion leading to molecular fragmentation. In order to be
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able to describe the nuclear configurations and their dynamics, we first need to understand the interactions that hold the atoms together in a molecule.

2.1 Nuclear potential energy surface

The precise arrangement of the atomic nuclei in space which is in equilibrium with the spatial distribution of electrons corresponds to a minimum of the total energy of the molecule.

The quantum mechanical model for the equilibrium structure of a molecule consisting of \( K \) nuclei (with masses \( M_k \) and charges \( Z_k e \)) and \( N \) electrons (mass \( m \), charge \( -e \)) in a state with total energy \( E \) is described by the Schrödinger equation:

\[
\hat{H} \Psi = E \Psi \quad (1)
\]

where the Hamiltonian, \( \hat{H} \) is the sum of the operator of the kinetic energy of all electrons and nuclei and the potential energy:

\[
\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 - \frac{\hbar^2}{2} \sum_{k=1}^{K} \frac{1}{M_k} \nabla_k^2 + V(R, r). \quad (2)
\]

In this equation the lower case letters denote electronic coordinates \( r_i \) and the upper-case letters denote nuclear coordinates \( R_k \). The potential energy \( V(R, r) \) which is a function of the spatial configuration of the nuclei and electrons can be written as a sum of three terms:

\[
V(R, r) = V_{\text{nucl,nucl}} + V_{\text{nucl,el}} + V_{\text{el,el}} = \frac{e^2}{4\pi\varepsilon_0} \left[ \sum_{k'<k}^{K} \sum_{k=1}^{K} \frac{Z_k Z_{k'}}{R_{k,k'}} - \sum_{i=1}^{N} \sum_{k=1}^{K} \frac{Z_k}{r_{i,k}} + \sum_{i>i'}^{N} \frac{1}{r_{i,i'}} \right] \quad (3)
\]

where \( R \) contains all nuclear coordinates written in the center of mass frame of the molecule \( R = (R_1, R_2, ..., R_K) \) and equivalently \( r = (r_1, r_2, ..., r_N) \). The abbreviations: \( R_{k,k'} = |R_k - R_{k'}| \), \( r_{i,k} = |r_i - R_k| \) and \( r_{i,i'} = |r_i - r_{i'}| \) are used to express the relative distances between electrons and nuclei. In this description all interactions relating to electronic or nuclear spins have been ignored.

The first term in the potential energy describes Coulomb repulsion between the nuclei, the second term Coulomb attraction between the electrons and the nuclei and the third term accounts for the mutual repulsion between the electrons.

Figure 1: Representation of the electrons and nuclei in the molecule’s center of mass frame with origin \( S \)

As long as the nuclear kinetic energy is small in comparison to electronic kinetic energy, we can treat it as a perturbation of the molecule with a rigid nuclear framework exhibiting zero kinetic energy. This means that the Hamiltonian from Eq.(2) can be rewritten as:

\[
\hat{H} = \hat{H}_0 + \hat{H}' \quad (4)
\]

Obtaining the exact solution of the time-independent Schrödinger equation for a molecular system is obviously a difficult task if we remember that even for a two-electron atom no analytical solution exists. That is why we introduce physically motivated approximations that lead to simplified solutions of the Schrödinger equation. The problem is reduced if we take into account that the electron mass is much smaller than that of the nuclei, while the interactions between the electrons and the nuclei are of comparable magnitude. As a consequence of the large mass difference between electrons and nuclei, the time scale for electron movement is much shorter than the one for the nuclear movement. This means that in the eyes of the electrons, the nuclei are stationary and as the nuclei move, the electrons react to nuclear position changes instantaneously.\(^3\),\(^6\)
where $\hat{H}_0 = \frac{-\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + V(\mathbf{R}, \mathbf{r})$, and $\hat{\mathcal{H}} = \frac{-\hbar^2}{2} \sum_{k=1}^{K} \frac{1}{M_k} \nabla_k^2$

The unperturbed Schrödinger equation:

$$\hat{H}_0 \varphi_n(\mathbf{r}, \mathbf{R}) = E_n^0(\mathbf{R}) \varphi_n(\mathbf{r}, \mathbf{R})$$

(5)

describes a molecule with a fixed nuclear configuration, \( \mathbf{R} \). The absolute square of the wavefunction \( \varphi_n(\mathbf{r}, \mathbf{R}) \) for an arbitrary fixed nuclear configuration gives the charge distributions of the electrons in the state \( n \) and energy \( E_n^0(\mathbf{R}) \), where \( n \) denotes the different electronic states of the rigid molecule. One important thing in the solution of the unperturbed Hamiltonian is that the electronic coordinates are the variable argument of \( \varphi_n(\mathbf{r}, \mathbf{R}) \) and the nuclear coordinates are fixed. The functions \( \varphi_n(\mathbf{r}, \mathbf{R}) \) can be chosen such that they form a complete orthogonal set at each \( \mathbf{R} \). In this case, every solution \( \Psi(\mathbf{R}, \mathbf{r}) \) of the complete Schrödinger equation (expressed with Eq.(2)), can be written as an infinite sum of these functions:

$$\Psi(\mathbf{R}, \mathbf{r}) = \sum_m \chi_m(\mathbf{R}) \varphi_m(\mathbf{r}, \mathbf{R})$$

(6)

where the expansion coefficients \( \chi_m(\mathbf{R}) \) represent particular nuclear configuration. In case of a stable molecule where the nuclear kinetic energy is small compared to the electronic kinetic energy, the motion of the electrons can be considered independently from the nuclear motion (BO (Born-Oppenheimer) approximation) and the sum in the equation above reduces to a single term. Within the Born-Oppenheimer approximation, one can define electronic states \( |n\rangle \) and nuclear states \( |i\rangle \) independently, so the total wavefunction of a molecular state can be written as their product:

$$|n, i\rangle = \Psi_{n,i}(\mathbf{R}, \mathbf{r}) = \chi_i(\mathbf{R}) \varphi_n(\mathbf{R}, \mathbf{r})$$

(7)

Here, \( \varphi_n \) is one of the eigenstates of the Hamiltonian \( \hat{H}_0 \) and represents an orbital in which the electron moves. Atomic orbitals contain electrons ascribed to a single atom while molecular orbitals, that contain the valence electrons between atoms, can surround several atoms. Inside the molecular orbital theory, molecular orbitals can be calculated as a linear combination of the atomic orbitals of the valence electrons:

$$\varphi_n = \sum_r c_{rn} \psi_r$$

(8)

where \( c_{rn} \) is the weight of the contributions of the atomic orbitals to the molecular orbital, \( \psi_r \) is the atomic orbital and \( \varphi_n \) is the molecular orbital. In principle, we should use an infinite number of atomic orbitals for precise recreation of the molecular orbital, but in practice only a final basis set is used. Additionally, we must assure that the atomic orbitals included in the sum are real and normalized to 1.

The optimal values for the coefficients \( c_{rn} \) is found by applying the variational principle for the energy of the system.\([3],[4]\)

If we try to solve the complete Schrödinger equation with Eq.(7) as ansatz, as a result we get two decoupled equations:

$$\hat{H}_0 \varphi_n(\mathbf{r}) = E_n^0(\mathbf{R}) \varphi_n(\mathbf{r}, \mathbf{R})$$

(9)

$$\hat{\mathcal{H}} + E_n^0(\mathbf{R}) \chi_n(\mathbf{R}) = (T_{\text{ncl}} + U_n(\mathbf{R})) \chi_n(\mathbf{R}) = E_n \chi_n(\mathbf{R})$$

(10)

From these equations one sees that \( E_n^0(\mathbf{R}) \) represents the potential in which the nuclei move, \( U_n(\mathbf{R}) \). The potential for a selected type \( n \) of electronic wavefunction is represented by a potential energy surface in the space of nuclear coordinates.

The two general types of the potential energy curve for the simplest diatomic molecule are shown in Figure 1. The graph on the left side depicts a potential energy curve supports bound molecular states with negative energy. At large internuclear distances the curve flattens out and in this so-called dissociation limit the molecule is no longer bound, being instead the two separate atoms. The dissociation energy equals the difference between the dissociation limit (zero energy) and the initial bound state energy in the potential well. The potential energy curve may not have a bound state. The typical shape of these curves is decaying and has no minima, like in the graph on the right side of Fig.2.

The potential energy surface (PES) description offers very intuitive approach to understanding and further investigation of the molecular dynamics. By studying the characteristic points and shape of the PES one can determine bond lengths (position of the potential minimum) and predict molecular fragmentation pattern.\([5],[6],[7]\)
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The general form of the electronic energy $U(R)$ for a diatomic molecule. The internuclear distance $R_0$ at minimum is called equilibrium distance.

The general form of the repulsive electronic energy $U(R)$ giving no bound states of a diatomic molecule.

Figure 2: Two different types of nuclear potential energy curves

2.2 Experimental studies of the PES: Heisenberg’s uncertainty principle and wave packets

For experimental studies of the shape of the PES which determines the dynamics of breaking and creation of molecular bonds we need to be able to make time resolved measurements of the nuclear motion. The speed of the nucleus is around 1 km/s and in order to record the motion of the atoms over a distance of 0.1 nm (the typical bond length), the time resolution required is around 100 fs. In order to be able to take snapshots of the dynamics of such fast process the light pulses must have time duration on a scale comparable to the time scale of the nuclear motion. Improvements in the laser technology have resulted in the ability to produce light pulses with duration comparable to the time resolution required for probing the atomic motion. That enabled experimental groups to build measuring systems (that will be described below) capable of probing the atomic motion by taking snapshots of the molecular dynamics of the excited molecular system. Each snapshot of the atomic motion represents a measurement of the degree of localization of the system in space created in a very short time. Such measurement must be consistent with the Heisenberg uncertainty principle:

$$\Delta t \Delta E \geq \frac{\hbar}{2}$$

In order to understand how does this relationship applies to our system we will examine the effect of photon absorption on a molecule.

For simplicity, let’s consider a diatomic molecule with internuclear separation $R$. We assume that at $t = 0$ the excitation takes place from the electronic ground state into a bound state (excited electronic state of the molecule that doesn’t give the repulsive nuclear potential). The heavy nuclei do not change their positions or momenta during electronic transition. As a consequence of the instantaneous excitation process the nuclear wavefunction, $\chi_0$, at the moment of transition does not change its initial shape. However, the molecular system finds itself now in a new potential surface - the one of the excited electronic state. Such a vertical transition of the molecular wavefunction upon photon absorption is known as Franck - Condon principle.

Figure 3: (a) Evolution of the wavepacket in the excited electronic state. The time duration is given in femtoseconds (b) Schematic illustration of the potentials in the lower and upper electronic states.
In the new potential that nuclear wavefunction can be described as a coherent superposition of eigenfunctions of the excited state potential - a wavepacket. When such wavepacket is created it begins to move under the influence of the intramolecular forces governed by the electronic redistribution. The distribution of eigenstates composing the wavepacket is determined by the shape of the amplitude of the time-dependent EM field.

Because of the Heisenberg uncertainty principle, the shorter the pulse the more eigenstates contribute to the wavepacket. Such a coherent superposition is not an eigenstate of the excited-state potential, so it is not stationary in time. The time dependence of the nuclear wavefunction in the excited state is therefore given by:

\[ \chi(t) = \sum_{n=0} a_n e^{-i \frac{E_n}{\hbar} t} \chi_n \]  

where \( a_n \) are time-independent weights of nuclear wavefunctions \( \chi_n \) of the excited state potential, simply given by overlap integral \( \langle \chi_0 | \chi_n \rangle \).

If one calculates the probability for a particular inter-nuclear distance \( R \) in the excited state:

\[ |\chi|^2 = \left| \sum_n a_n \chi_n e^{-i \frac{E_n}{\hbar} t} \right| \left| \sum_m a_m^* \chi_m e^{i \frac{E_m}{\hbar} t} \right| \]  

One can see immediately that cross-terms \( m \neq n \) in this product are not time independent (the phase factors do not cancel like in the case of stationary eigenstates), but oscillate at the frequencies determined by the energy differences \( E_n - E_m \). The expected outcome of a nuclear position measurement therefore changes in time which means that the molecular system is in motion. The nature of the nuclear motion which can be oscillatory or dissociative, is determined by the shape of the excited potential energy surface of the molecule. By taking snapshots of this motion, one can indirectly measure the shape of the PES.[4],[7],[8],[9]

### 3 Time-resolved measurements of the molecular dynamics

#### 3.1 The pump-probe method

Direct measurement of the temporal evolution of a dynamic molecular system is not possible by the use of electrical methods and other non-optical techniques. The use of specialized photodetectors such as streak cameras or avalanche photodiodes with picosecond or even several hundred femtosecond resolution can not resolve such fast events. This fact has motivated experimental groups to find techniques that depend on two or more ultrashort pulses to initiate and monitor a dynamical process in which the time resolution in the resulting signal does not depend crucially on the detection method. The most commonly used arrangement for this kind of measurements is the pump-probe set-up. The time resolution of the pump-probe experiments depends on the time delay between the pump and the probe laser pulses and not on the temporal response and time definition of the detector.
In order to produce the pump-probe pulses, the light from a pulsed laser is split by partially reflective mirror into two parts with equal wavelength: pump beam with intensity of about 90% of the initial pulse and probe beam of about 10% of the initial pulse. The fs time delay of the probe relative to the pump pulse is usually achieved by an extra optical path of the probe beam that can be of variable length. For typical optical length difference of 1 µm the probe pulse is delayed for 3,3 fs. These kind of systems use pulse lasers that are able to produce pulses as short as 5-6 fs and the time-delay jitter of such pump-probe setup can be better than a single femtosecond. By measuring the specific signal induced by the probe hitting the molecular system at certain time after the pump and repeating the measurements by varying the time delay between the pulses, one can determine the temporal dynamics of the molecular excitation in a controlled way.\[7],[8],[9]

3.2 Pump-probe measurements of the dynamics of molecular dissociation

In the pump-probe experiments, the dynamics of bond breaking is observed by measuring the absorption properties of the molecular fragments depending on both the time and wavelength. One of the ways to study the dynamics of bond breaking is by observing the dynamics of an elementary process such as:

\[ ABC^* \rightarrow [A...BC]^* \rightarrow A + BC \] (14)

where a single chemical bond is broken (\(^*\) denotes an excited state). During the period of bond breaking which we have previously estimated to be of order of femtoseconds, the system passes through transition states (labelled with \(\ddagger\)). The transition state of a reaction is an irreversible nuclear configuration, i.e. once the molecular system has achieved it its temporal evolution leads to formation of fragments.

Through a step-by-step analysis of the photoinduced fragmentation of an ABC molecule I will try to give a general description of the basics steps needed for measuring the molecular dissociation dynamics. In the analysis of this process the only relevant configurational parameter is the internuclear distance of the fragments in the center of mass frame, \(R\). Every angular dependence is excluded. Such molecules have simple PES's (shown in Fig.6) that are typical of many real molecules undergoing bond breaking. Initially, the molecule is in its lowest potential surface \(V_0\) that has a well-defined minimum which is located at an equilibrium internuclear distance \(R_e\). The measurement begins with an ultra-fast laser pulse, with wavelength \(\lambda_1 \equiv \lambda_{\text{pump}}\), which initiates the reaction of photodissociation. All times are measured relatively to the temporal midpoint of this pump pulse which defines the "zero of time". The distance between fragments at \(t = 0\) is defined as the initial internuclear separation \(R_0\).

In general \(R_0 \neq R_e\) and the deviation of the molecule from the equilibrium internuclear distance \(R_e\) when the molecule is at thermodynamic equilibrium is typically small. The absorption of the photon is substantial only if the difference in the potentials of the two surfaces at \(R_0\) is nearly equal to the energy of the pump photon:

\[ V_1(R_0) - V_0(R_0) \approx \frac{hc}{\lambda_1} \] (15)

Absorption of the photon involves the instantaneous vertical transition of the molecule from a lower lying PES, to an excited PES, \(V_1\).

The excited molecule prepared by the pump pulse at \(t = 0\) will evolve for \(t > 0\). The evolution of the wavepacket is entirely determined by the shape of the excited-state PES. After the molecule is allowed to evolve for some time delay, \(t = \tau\), it is irradiated by the probe pulse, with wavelength \(\lambda_2 \equiv \lambda_{\text{probe}}\). The probe pulse will only be absorbed if the configuration of the system at time \(\tau\) is appropriate for a transition from \(V_1\) to a highly
defined nuclear configuration at path delay as described above provides the required high degree of timing precision. Of equal importance is well-resolution for all molecules in the ensemble. The use of pulses generated from the same source and an optical femtosecond precision and that the configuration of the atoms at $t = 0$ is precisely defined to subangstrom resolution for all molecules in the ensemble. We have separate atoms.

To achieve such synchronizations we must assure that the relative timing of pump and probe pulses are of femtosecond precision and that the configuration of the atoms at $t = 0$ is precisely defined to subangstrom resolution for all molecules in the ensemble. The use of pulses generated from the same source and an optical path delay as described above provides the required high degree of timing precision. Of equal importance is well-defined nuclear configuration at $t = 0$. This definition is naturally realized in a low temperature environment because the femtosecond pump pulse launches essentially all members of the molecular ensemble from their ground states.\[7],[8],[10],[11]\]

4 The dissociation dynamics of sodium iodide (NaI)

Bellow, I present one of the experiments performed more than twenty years ago by a research group from the Laboratory of Chemical Physics at California Institute of Technology. I chose to describe this experiment because it represents a relatively simple but still non-trivial example for understanding the time evolution of the atomic motion during dissociation. The photoinduced dissociation reaction of NaI investigated in this experiment, was measured in real time by femtosecond pump-probe spectroscopy.

4.1 Short theoretical background

The bond breaking that was discussed so far was explained by purely dissociative PESs. However in the process of fragmentation, the molecular system(wavepacket) may encounter a well in the PES. In that case trapping can occur and a resonant behaviour of the wavepacket can be observed. Alkali metal-halogen dissociation reactions are perfect example for studies of such dissociation behaviour, because in this case there is crossing of the ionic ground potential energy surface with the lowest excited covalent potential energy surfaces.

The crossing of the potential energy surfaces arises from the fact that the energy required for ion formation (Na$^+$ + I$^-$) is larger than the energy for separation of the sodium iodide into neutral atoms (Na + I). Consequently, the ionic ground state potential energy surface has higher energy at large internuclear distances compared to the energy of the lowest excited covalent potential energy surfaces. The energy difference between these potential energy surfaces in the limit of large internuclear distances is given by the difference between the ionization energy of the alkali atom (Na) and the electron affinity of the halogen atom (I). It must be emphasised that at distances larger than several angstroms (the typical bond length), we can no longer talk about a single molecule because we have separate atoms.\[13\]

The temporal evolution of the dissociation reaction near the crossing point can no longer be described by the Hamiltonian within the BO approximation, because the nuclear and electronic motion become coupled (the solution of the Schrodinger equation must now be written as: $\Psi_{n,i}(R, r) = \sum_m \chi_{m}(R)\varphi_{m}(r, R)$ where $m$ is finite) and the energy of the system at that point cannot be determined. For an accurate description of the system at this point, we must use perturbative expansion to recalculate the energy difference between PES. In that way we can calculate the interaction strength between the potential surfaces which depends on the coupling between nuclear and electronic wavefunctions.

In the case where the interaction is very weak and the modification of PES is very small so the dissociation path of the molecule is confined to the initial potential energy surface upon which it was prepared. If the excited PES, $V_2$. Those configurations which allow for absorption of the probe photon depend on the difference between the appropriate PES’s as a function of the internuclear separation, $V_2(R) − V_1(R)$, the frequency and spectral width of the probe pulse.

The signal that is usually recorded with photodetector (time resolution in the order of ns) is the level of absorption of the probe pulse by the wavepacket as a function of the time delay between pump and probe, $\tau$. Typically, the measurement of the signal is made when $\lambda_2$ is tuned to the absorption wavelength of the free fragment, $\lambda_2^{\text{free}}$ and also at several different wavelengths absorbed by the transition states, $\lambda_2^{\text{‡}}$ denotes the transition-state region of $R$. The recorded signal is used for construction of a surface of measurements $A(t, \lambda_2^{\text{‡}}, \lambda_1^{\text{‡}(a)}, \lambda_1^{\text{‡}(b)}, \ldots, \lambda_1^{\text{‡}})$ from which we can deduce the dynamics of the system and the PES involved in the process of fragmentation. These measurements are not performed on a single molecule, but on many independent molecules. In order to obtain a clear image of the dissociation process without blurring the measurement signal, one needs to ensure in some way that the motion of the molecular ensemble is temporally and spatially synchronized. The synchronization of the motion of many independent molecules must be made in a way so that all have reached a similar point in the course of their configurational evolution when the probe pulse arrives to capture their nuclear configuration at some particular moment.
interaction between the potential energy surfaces is relatively strong, a trapping well can be formed. The temporal evolution of the molecule in this case is described as a periodical movement within the potential well. The experimentally observed behaviour of NaI fragmentation was expected to be between these two limits.

Figure 7: The figure on the left represents the potential energy surfaces involved in the dissociation reaction of NaI: the ground ionic state and the two excited covalent states. The highest one represents PES of electronically excited Na.\textsuperscript{11} The right figure depicts the formation of a well on the excited state PES, because of an avoided crossing between covalent and ionic PES.\textsuperscript{15}

4.2 Description of the experiment

The pump-probe setup used for studying NaI dissociation was equipped with a colliding pulse mode-locked ring dye laser (CPM) that produced the femtosecond pulses that were amplified by Nd:YAG pumped pulsed dye amplifier (PDA). The output pulses had energy of about 30 µJ and wavelength centred at about 620 nm. The temporal pulse width was measured to be 60 fs and had repetition rate of 20 Hz. For measuring the shape of the PESs involved in the dissociation, tunable radiation of the pump and probe wavelengths was required. The different wavelengths were generated by non-linear methods (doubling and mixing frequency crystals were used). With the use of this techniques a pump pulse wavelength in the range from 235 nm to 388 nm was produced and the duration of the pulse varied from 100 fs to 200 fs. By tuning the pump wavelength, one is changing the total available energy for the reaction, thereby preparing different wavepackets on the covalent potential. The probe pulse was tuned to measure either the resonant absorption of the free Na D-lines (589 nm and 589.6 nm) or the absorption of the transition states.

Figure 8: The setup for generation of the pump/probe pulses. The femtosecond pulses are generated in the CPM laser and are amplified in a pulsed dye amplifier. After the amplifier, the pulses are broadened temporally, which is compensated for with recompression methods (prisms arrangement). The pump and probe pulses are generated through a variety of frequency conversion schemes and are directed into the sample chamber.\textsuperscript{13}

The effective tuning range of the probe for which a signal could be obtained was from 550 nm to 787 nm. By varying the probe wavelength, one can effectively view the dynamics of the dissociative process at different positions along the reaction coordinate. The pump and the probe pulses were delayed in time relative to one another by a Michelson interferometer arrangement. The typical delay between the pulses ranged from -100 fs to 1000 fs. The beams were colinearly recombined and focused into an 8 cm long vacuum-sealed quartz cell which contained pure NaI. Before the measurements, the sample was heated to 400°C under vacuum.
(pressure was less than one mPa) for approximately eight hours in order for the excess water to be removed.
For the experiment, the cell was heated in an oven to a temperature of 650°C in order to obtain molecular gas
form of the sample. In these conditions, the vapour pressure of NaI was measured to be in the range of 130 mbar.

Because of the relatively high temperature inside the cell additional Na fragments were produced by thermal
dissociation too, but there was no evidence of any thermal contribution because the variation of the oven
temperature in a range of approximately 100°C did not affected the signal of the resonant absorption of the
probe pulse.

The laser induced fluorescence (LIF) from the Na atoms was collected orthogonal to the pump/probe pulses
by an arrangement of lenses. The fluorescence of the Na atoms (with decay-time of 16 ns), was detected
with photomultiplier tubes. The detected fluorescence signal from the exited species was then integrated for a
sufficient length of time to yield a measure of the total photon intensity.\textsuperscript{13}

4.3 Experimental results
The experimental results from the probing the transition state of NaI (at $\lambda_{\text{probe}}$) showed a striking oscillatory
behaviour that persisted for about 10 ps. This oscillation is a manifestation of the propagation of the wavepacket
(generated by the pump) back and forth across the potential well. The period of this oscillation was measured
to be about 1 ps, corresponding to frequency of about 1 THz. The dumpling amplitude of the oscillating signal
corresponds to the portion of the molecules that have dissociated through one of the available channels. The
Fig.9 shows the data measured with varying probe wavelength.

![Figure 9](image)

(a) Measurement results for NaI for a broad range of probe
wavelengths
(b) Measurement results for NaI as a function of probe
wavelengths: a)575 nm; b)580 nm; c)590 nm and d) 615 nm

Figure 9: The data displayed in the two figures the pump was centered at 307nm, had a bandwidth of 3 nm and
a pulse duration of 50 fs. The tunable probe had a 10 nm bandwidth and a pulse duration of approximately
250 fs.\textsuperscript{11}

When the probe was tuned on the wavelength for resonant absorption of the free Na doublet the signal showed
an initial sharp rise, followed by a series of rising plateaus which showed the same temporal separation as the
peaks in the off-resonance data. In this channel the probe actually measured the leakage of the wavepacket each
time it passed through the interaction region. By variation of the pump wavelength it was measured that the oscillation period of the wavepacket changes. This is because changing the pump wavelength changes the energy available to the molecule for reaction. When the pump pulse was tuned to the longer (shorter) wavelengths it was observed that the oscillation period decreases (increases) and that with longer (shorter) wavelengths of pump pulses the dumping of the wavepacket oscillations decreases (increases). This behaviour can be expected because the variation of the available energy also changes the probability for escaping the potential barrier at large internuclear distances.

![Graph](image1)

From these measurements it can be concluded that the predicted appearance of an oscillation in the measurement results was observed which is an indication of the strong interaction between potential energy surfaces at the crossing point. The measurements obtained by variation of the pump/probe pulses contributed to characterization of the dynamics of the oscillatory dissociation of NaI.

5 Conclusion

In this seminar I presented an elementary description of the basic concepts included in the process of observation and measurements of events related to molecular relaxation on a femtosecond time-scale. Observation of femtosecond processes is not necessary limited to the studies of systems such as the two - atom system used as an example above. Techniques similar to the one that I described have been applied to problems such as revealing the mechanism for energy conversion in chlorophyll (photosynthesis) and understanding the way human eyes detect light. These examples show that femtosecond processes can be observed in all phases of matter and in much more complex systems. Today, with the construction of pulse lasers that produce attosecond pulses, measurements with increasingly higher time resolution can be obtained. Such instruments enable us time resolved observation of extremely fast events such as the movement of the electron during the ionisation of an atom (TU Vienna, 2012[14]) which was measured with resolution of less than ten attoseconds.
References


[5] www.chm.bris.ac.uk/ Potential energy surfaces for Diatomic Molecules


