Photoinduced dynamics of NO$_2$ and Tetrakis molecules using Velocity Map Imaging
Photoinduced dynamics of NO$_2$ and Tetrakis molecules using Velocity Map Imaging

een wetenschappelijke proeve op het gebied der
Natuurwetenschappen, Wiskunde en Informatica

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de
Radboud Universiteit Nijmegen op gezag van de
Rector Magnificus prof. dr. C.W.P.M. Blom, volgens besluit
van het College van Decanen in het openbaar te verdedigen
op woensdag 5 oktober 2005 des morgens om 10.30 uur precies

door

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Chapter I

Introduction

This thesis describes studies of the photoinduced dynamics of the molecules NO₂-nitrogen dioxide and of C₁₀H₂₄N₄-tetrakis (dimethylamino)ethylene.

This chapter will introduce the motivations for these studies and presents some of the necessary background information for these two molecules.

1.1. Photoinduced dynamics

Molecular quantum dynamics (MQD) is a broad subject in physics, and one that involves not only a change in electronic configuration, but also a change in the nuclear, vibrational and rotational motion associated with a molecule [1-10]. In the past MQD has predominantly been focused by theoretical studies, which have been possible since the birth of quantum mechanics, with practical studies being somewhat limited due to the lack of effective experimental tools. However, recently more extensive experimental studies have been made possible with the development of new technology. The
preparation/synthesis of novel compounds, the refinement of theories governing molecular composition/structure, and the subsequent determination of such structure provide a challenge to both chemical physicists and physical chemists who wish to control the route in which a chemical reaction takes and understand the energy/dynamics involved in such a reaction.

As a definition, molecular dynamics [11] is principally concerned with inter- and intra-molecular motions that occur in the elementary act of chemical change, studying the change and details of the relationships between the quantum states of the reactant molecules and those of the product molecules. After the molecules react, which usually involves the creation/destruction of chemical bonds, they reorganize themselves into another set of atoms and/or molecules (i.e. reaction products) which may then react further. The fundamental goal of molecular reaction dynamics therefore is to understand the elementary steps which make up a chemical reaction by following the time evolution of every individual reaction step, as far as is possible [12].

In all the studies described in this thesis a molecule typically absorbs a photon which causes it to exist in a short lived excited state. Such a molecule can subsequently dissociate or absorb further photons and eventually ionise if there is sufficient energy involved. Figure 1 gives an overview of the many processes that can take place from this excited state. These processes are described in detail in sections I.1.1. and 1.1.4.

I.1.1. Photofragment Translational Spectroscopy

The interaction of radiation with matter is of great interest in modern physics. There are a number of different ways in which photo-reactive molecules respond to incident radiation. Here I introduce a theoretical molecule, designated as \(ABC\), for illustrative purposes. After absorption of one or more photons (\(h\nu\)) the \(ABC\) molecule in the ground state, becomes the excited molecule \(ABC^*\), which may then undergo various reactions [13]. If the photon energy exceeds the binding energy of the molecule, dissociation can occur, resulting in the production of fragments. Figure 1 shows the potential energy
curves relevant to the types of dissociation which may occur upon excitation of simple polyatomic molecules.

The most common form of dissociation for a triatomic molecule (e.g. \(ABC\)) is the dissociation at the weakest bond as shown in reaction 1.1. (where, in this instance, the \(B-C\) bond is weaker than \(A-B\) bond). Another form of dissociation is photo-ionization, where an electron has enough energy to escape from the highest occupied molecular orbital leaving behind a positive ion as shown in reaction 1.2. The third possibility is a cumulative dissociation and ionization process as shown in reaction 1.3. The order of these processes is governed by the intensity of the incident energy.

\[
\begin{align*}
ABC + nh\nu &\rightarrow ABC^* \rightarrow AB + C & \text{photodissociation} \\
ABC^* + e^- &\rightarrow AB^+ + C + e^- & \text{photoionization} \\
&\rightarrow AB^+ + C + e^- & \text{dissociative ionization}
\end{align*}
\]

All three of these processes are equally important for the work presented in this thesis therefore I will discuss each type of reaction in the order in which they have been presented above. During the photodissociation process the bond between atoms B-C is broken and two neutrals fragments fly apart. The energy at least required to break this bond is called the dissociation energy \(D_0\), where the zero indicates dissociation from the lowest possible rotational level of the ground vibrational state \((v=0)\). If the intermediate state of \(ABC^*\) is a repulsive one, the molecule will dissociate immediately and this process is called \textit{direct photodissociation} (see figure 1). Otherwise, if the molecule is excited to a bound state, dissociation can occur if the intermediate state \(ABC^*\) couples to a repulsive state. In this case the process takes more time before \(ABC^*\) fragments and is called \textit{indirect photodissociation} or \textit{predissociation}.

The photodissociation reaction event occurs under the constraint of the conservation of both energy and angular momentum. When the bond dissociation energy is \(D_0\), the available energy \(E_{AVL}= \nu-D_0\) is distributed among the “\textit{external}” (translational) energy \(E_t\) and “\textit{internal energy}” \(E_{int}\) of the fragments. The internal energy is shared among electronic \(E_e\), vibrational \(E_v\), rotational energy \(E_r\), and possible spin fine structure and A-type doubling of the photofragments.
Figure 1: Potential energy curves relevant to various decay processes: $dD/iD$ - direct/indirect dissociation, $dI/iI$ – direct/indirect ionization and $dDI/iDI$ - direct/indirect dissociative ionisation.

The way in which the available energy $E_{AVL}$ is distributed among “external” and “internal” energy is known as energy disposal.

$$E_{AVL}^{(ABC)} = E_{int}^{(AB)} + E_{int}^{(C)} + E_I^{(AB)} + E_I^{(C)}$$

(1.4)
In a two-body dissociation reaction, the translational (kinetic) energy partitioning among the fragments can be determined using the conservation of linear momentum. Consider the process described in reaction (1.1):

\[ ABC + nhv \rightarrow ABC^* \rightarrow AB + C + E_t \]  

(1.5)

where \( E_t = E_t^{(AB)} + E_t^{(C)} \).

When neglecting the thermal motion of the parent molecule ABC, conservation of momentum relates the velocity vectors of the nascent fragments as:

\[ m^{(AB)} \nu^{(AB)} + m^{(C)} \nu^{(C)} = 0 \]  

(1.6)

From last two equations results:

\[ \nu^{(AB)} = \frac{m^{(C)}}{m^{(AB)}} \]  

(1.7)

Translational energy is partitioned for each fragment as:

\[ E_t^{(AB)} = \frac{m^{(c)}}{M} E_t \]  

(1.8)

\[ E_t^{(C)} = \frac{m^{(AB)}}{M} E_t \]  

(1.9)

with \( M = m^{(AB)} + m^{(C)} \).

Another type of dissociation is the simultaneous breaking of two bonds and the formation of a new bond:

\[ ABC \rightarrow AC + B \]  

(1.10)

This type of dissociation is common in the vacuum ultraviolet. Also common for photolysis in the vacuum ultraviolet is the three atom production.

\[ ABC \rightarrow A + B + C \]  

(1.11)

Another important factor is the photon density. For low photon densities the molecule can usually only absorb one photon (as in the dissociation processes described above). However, when higher densities are applied multi-photon excitation or ionization may occur (reaction 1.2). Here the energy of the absorbed photons can be of a sufficient magnitude for an electron to be ejected from the molecule, forming ABC\(^+\). Usually the minimum energy necessary for such an ionisation process is called ionization potential (IP). For a direct ionisation the electron leaves the molecule
immediately and usually this process is occurred via an intermediate state. For an indirect ionisation (or autoionization) the molecule is brought to an excited state above ionisation potential and can subsequently decay into the ionisation continuum.

The dissociative ionisation process requires even more energy to become deposited into the target molecule so that the bond of the ion ABC$^+$ may be broken. The direct dissociative ionisation takes place when the photoexcited intermediate state of ABC$^*$ is a repulsive ion state. Otherwise the process is called indirect dissociative ionisation where a highly excited intermediate state ABC$^{**}$ is involved. The ionisation and the dissociative ionisation processes are described in more detail in section I.1.4.

Some further decay mechanisms occur by the interaction of the photon field with molecules that do not result in the fragmentation of the molecules. If the intermediate state ABC$^*$ does not decay via the fragmentation process, the molecule can return to the ground state by either a radiative or non-radiative transition.

### I.1.2. Angular distribution

In our experiments the parent molecule which is excited by laser radiation explodes into a number of recoiling photofragments. This process is described by equation (1.5) above, but for simplicity I choose a theoretical diatom named AB, where the mass A > mass B. In Fig.2a, the dissociation events sends fragment A upwards and fragment B downwards; both events shown in a) are independent possible processes with different ejection directions. In b), the possible sum over a large number of events is indicated, all caused by photons with a perpendicular polarisation direction.

If we assume that all events start at the same point in space $(x, y, z=0,0,0; \Delta x, \Delta y, \Delta z=0,0,0)$, with zero initial velocity for the parent molecule $(v_x, v_y, v_z = 0,0,0, $ $\Delta v_x, \Delta v_y, \Delta v_z = 0,0,0)$ then each dissociation event will yield particles with identical speed but varying direction. This creates the Newton spheres (fig. 2(a), (b)). The size of the Newton sphere is directly proportional to the fragment’s speed.
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Figure 2. Newton spheres with two spherical coordinates \( r_1 \) and \( r_2 \), \( \theta \)-the polar angle defined with respect to the z axis and \( \varphi \) - the azimuthal angle. Two events are shown in (a) with equal and opposite momentum; (b) the summing of a large number of events. Here \( \vec{E} \): polarisation vector of the exciting laser light and \( \vec{\mu} \): the transition dipole moment vector.

By using linearly polarised light (\( \vec{E} \)), the angular distribution is likely to be anisotropic along the laser polarisation and several other vectors of interest can be measured in correlation with \( \vec{E} \) [14, 19]. The vectors of interest due to the vector correlation are: \( \vec{E}_0 \) – the polarisation vector of the laser light (chosen to be parallel to the z direction of the laboratory frame \( \vec{E}_0 = (|E_0| \vec{e}_z) \), \( \vec{\mu} \) - the transition dipole moment vector of the diatom which is either parallel or perpendicular to the diatom axis, \( \vec{v} \) – the recoil velocity of the fragments, \( \vec{I} \) – the rotational angular momentum of the atom (fig. 2).

The angular distributions depend on both the laser polarisation and the symmetries of the electronic states that are involved in the dissociation process. The transition dipole of an allowed one photon transition between two electronic states of a diatom is either parallel or perpendicular to the diatom axis, depending on the symmetry properties of
the initial and the final state. The general equation of the photofragment angular distribution in one photon dissociation process can be described with the formula obtained by Zare and Herschbach [5,6]:

\[
I(\theta) = \frac{1}{4\pi} \left[ 1 + \beta P_2(\cos \theta) \right]
\]

(1.12)

where \( \theta \) is the polar angle between the polarisation vector of the laser light and the recoil velocity of the fragment and \( P_2 \) is the second order Legendre polynomial.

For example, the \( \Sigma \rightarrow \Sigma \) and \( \Pi \rightarrow \Pi \) electronic transition of a diatom are parallel transitions, but \( \Pi \rightarrow \Sigma \) is a perpendicular transition. A transition dipole moment directed along the molecular axis (\( \mu_x = \mu_y = 0 \), \( \mu_z \neq 0 \)) corresponds in the case of weak spin orbit coupling to a transition in which the projection of the orbital angular momentum on the diatom axis (\( L_z \)) is conserved (\( \Delta \Lambda=0 \)). This type of transition is called a parallel transition, characterised by \( \beta=2 \) and an angular distribution \( I(\theta) \) that is proportional to \( \cos^2 \theta \). Figure 2 shows the Newton sphere for a parallel transition. A transition dipole moment perpendicular to the molecular axis correlates with the situation where \( \Delta \Lambda=\pm 1 \) and is therefore called perpendicular transition. It corresponds to \( \beta=-1 \) and the angular distribution is proportional to \( \sin^2 \theta \). An isotropic distribution is characterised by \( \beta=0 \). In general, the angular distribution of the recoiling fragments is normally expanded in a series of Legendre polynomials.

Figure 3. Two photoelectrons images reveal the angular distribution; left image: polar distribution-p wave, \( \beta=2 \); right image: coherent combination of s and d wave yielding \( \beta=-1 \).
The angular distribution of the photoelectrons with respect to the polarisation direction is a measure of the inherent anisotropy of the photoionisation process and reflects the nature of the orbital from which the electron is ejected.

For example, if an s orbital is ionised, an electron image with a polar distribution ($p\ \text{wave}$) corresponding to $\beta=2$ results; the situation becomes much more complicated for ejection of $l>0$ electrons. For p orbital ionisation, three situations can arise: an electron image with an isotropic distribution ($s\ \text{wave}$) corresponding to $\beta=0$, an electron image four lobe-shaped ($d\ \text{wave}$); interference effects can take place between the $s$ and $d\ \text{wave}$ yielding, for example, $\beta=-1$ (fig. 3).

1.1.3. Resonance enhanced multiphoton ionisation (REMPI)

Highly sensitive detection of photofragments is possible with modern detection techniques if the fragments are ionized. Single photon ionization requires a short-wavelength (UV or VUV) photon. The advent of intense nanosecond laser pulses has made multiphoton ionization (MPI) possible even for visible laser light. The easiest way to achieve ionisation using visible – UV photons is by using Resonance Enhanced Multiphoton Ionisation (REMPI). In the most common form of REMPI a neutral molecule absorbs one or more photons from a laser field and is excited to an intermediate electronic state. If the photon flux in the laser field is high enough the electronically excited molecule can then absorb additional photons sufficient to excite the molecule above its ionisation potential (IP). The ionisation process is usually very rapid and normally occurs immediately if the energy of the absorbed photons exceeds the IP. The ions are generally produced in a Franck-Condon distribution of internal energy states, along with photoelectrons that carry away the excess energy, although in favourable cases state selected ions can also be produced [17].

The power of the technique lies in the fact that the first excitation step is a resonant process.
Therefore, only molecules for which the laser frequency matches an allowed ro-vibrational transition frequency between the two molecular electronic states are subsequently ionised. This means that by tuning the laser frequency one can state-selectively (with respect to the initial state) ionise the molecule. It should be noted, however, that REMPI is not immune to unwanted side effects.

For example, it is not unusual for the REMPI process to compete with other (non-resonant) multi-photon processes, some of which can lead to fragmentation and the production of “unwanted” ions. It is common to describe various multi-photon ionisation schemes by the number of photons needed to reach the intermediate state plus the number needed to subsequently ionise the molecule. Thus in a 2+1 ionisation scheme (fig. 4) a two-photon process would be needed to excite the atom or molecule to some stable electronically excited state from which the further absorption of another photon
from the laser field would take the atom or molecule above the onset of the ionisation continuum.

Two photon excitation occurs via a virtual level. Such virtual levels are very short lived ($<10^{-15}$s) and, if the molecule does not return to the ground state, the laser intensity must be high enough for two or more photons to be absorbed within the lifetime of the virtual level. The laser power needed for REMPI depends largely on the number of photons required to reach the resonant intermediate level. Ideally, the resonant intermediate level is a particular ro-vibrational level of a Rydberg electronic state. Since these states consist of a molecular core (the state is often stable) weakly interacting with an excited electron the state is often stable and there is a high probability that ionization will occur. The REMPI spectrum is then essentially the same as the laser excitation spectrum corresponding to the first step of resonant excitation.

### 1.1.4. Photoelectron imaging spectroscopy

As described in section 1.1.1., the interaction of radiation with molecules depends on the energy and density of the incident radiation. Equation (1.2) describes the photoionization process (see fig. 1). When a molecule in its ground state ionizes after the absorption of one or more photons with sufficient energy, an ion and an electron are formed; in the ionization process the electron carries away nearly all the kinetic energy due to the large difference in mass of the electron compared to the ion. Typical ionisation energies of the molecules studied in this thesis have a value of between 5.4-10 eV. Conservation of energy and linear momentum shows that the kinetic energy of the ejected electron ($E_{e}$) is directly related to the internal energy of the ion ($E_{ion,ion}$) by the following relationship:

$$E_{ion,ion} + nh\nu \approx IP + E_{e} + E_{int,ion}$$  \hspace{1cm} (1.13)

For direct ionisation the electron leaves the molecule immediately, on a $10^{-15}$ s time scale. In the process of indirect ionisation or autoionisation, the intermediate state of ABC$^*$ lies above the I.P. and can thereafter decay into the ionisation continuum. This process also occurs on a similar time scale.
The dissociative ionization (DI) process (1.3) is a combination of reactions (1.1) and (1.2). This reaction is different in that more than one chemical bond is broken to form three (or more) fragments. In this case the simple two-body mechanics used for describing the Newton spheres above are not valid. For this process to occur the incident photon energy needs to be higher than for the other two processes so as to both ionise the ABC molecule and to break the B-C bond of the ABC⁺ ion. When the photoexcited intermediate state of ABC⁺ is a repulsive state, the process will be depicted as direct dissociative ionisation (dDI). Otherwise the process is called indirect dissociative ionisation (iDI). In case the intermediate state already has an energy $E > D_0$, one speaks of a superexcited state of the superexcited molecule ABC⁺⁺.

1.1.5. The Pump-Probe Technique

A pump-probe process can be viewed as a two laser interaction which involves the transfer of molecular population, usually from a ground state to an excited state of interest by the pump and then to a second state by the probe. The pump then induces a transfer of population to a higher excited state and the probe probes the dynamic of that state. Time-domain pump-probe techniques have been applied with great success (as recognised, for example, by a Nobel Prize in Chemistry for Prof. A. Zewail in 1999) in the study of ultra-fast molecular phenomena in biology, chemistry, and solid state science with temporal resolution in the $10^{-12}$-$10^{-15}$ s region. The ultra-fast temporal resolution is achieved by beam-splitting laser sources with very short pulse width and recombining the beams at the sample under investigation. By fine control of the optical paths of the two beams, the arrival of one beam can be delayed relative to the other by a chosen interval (1 mm ≈ 3.3 ps). The result is that molecular dynamics following arrival of the first excitation beam can be probed by the second beam with the optical delay. By varying the optical delay, molecular dynamics can be mapped at different times following the arrival of the initial excitation beam. In transient absorption studies, both lasers’ wavelengths are chosen to state selectively excite the sample. The first laser beam excites and depletes the molecules in the ground state. Later, the delayed second
laser beam arrives and probes the recovery of ground state population or the loss of excited state populations. Any dynamic processes affecting the return of molecules back to the ground state can then be studied by monitoring the effect of the probe laser beam.

Varying the optical delay between the pump and probe laser beams is key to the various implementations of pump-probe techniques in time-domain spectroscopy. Provided that mechanical stability of the optical components and measuring apparatus are well maintained, the temporal resolution of the time-domain approach is very high and is limited by the pulse width of the pulsed laser sources. Our laser pulse width is \(~100\) fs and ultra-fast molecular processes on this time-scale or slower can be probed using such lasers.

I.1.6. Polyatomic molecules, characterization of the conical intersection

The way in which the energy of the molecular system varies with small changes in its structure is specified by its potential energy surface (PES). A potential energy surface is a mathematical relationship linking molecular structure and the resultant energy. The validity of the energy surfaces for describing the molecular motion, equilibrium geometries, transition structures and reaction paths depend on the Born-Oppenheimer approximation to treat the motion of the nuclei separately from the motion of the electrons. Minima of the potential energy surface for the nuclei can be identified with the classical picture of the equilibrium structures of molecule, saddle points can be related to the transition states and reaction rates. The breakdown of the Born-Oppenheimer approximation is due to the motion of the atoms near the “intersections of potential surfaces belonging to a different electronic state and is often called a conical intersection” [22] (see fig. 5).

Conical intersections are defined as the intersection of two different potential energy surfaces when plotted along two coordinates. It has been shown that while intersection of potential surfaces belonging to two electronic states of different symmetry are common in the case of diatomic molecules, they are not forming a conical intersection. Conical intersections have been abundantly found in triatomic molecules as well as in
polyatomic molecules [23]. The system is expected to pass very quickly through conical intersection so their presence is characterised by:

- a very rapid decay (sub-picoseconds) of electronically excited states;
- lack of fluorescence (faster than fluorescence processes occur on the timescale $\text{ns-ns}$);
- rapid formation of products

A detailed understanding of the reaction pathway in the excited state manifold will increase our ability to design new and to control known photochemical reactions. Light is efficiently converted into chemical energy in biological molecules. The photosynthetic molecules often undergo cis-trans isomerisation and convert radiative energy into thermal energy on picosecond or shorter timescales. The advances of time resolved spectroscopy has provided a powerful tool to monitor reaction dynamics on the femtosecond timescale and made possible a direct observation of these processes.

Figure 5 presents a very schematic view of the course of the photochemical reaction. Following light absorption, the system is promoted to an excited state ($R \rightarrow h\nu \rightarrow R^*$). Photoproduct formation can then occur by adiabatic reaction ($R^* \rightarrow P'^*$) on the excited state surface (photochemical process) followed by emission ($P'^* \rightarrow h\nu \rightarrow P'$) or by adiabatic internal conversion to the ground state (photophysical process). However, the most common mechanism involves a non-adiabatic radiationless decay process which either regenerates the reactant $R$ (photophysical process) or generates new products $P$ or $P'$ (photochemical process). Electronically non-adiabatic processes (also called non-Born-Oppenheimer processes) are defined as those in which the electronic state changes non-radiatively during the dynamical event. There are many possible mechanisms for non-adiabatic radiationless decay. When real surface crossings exist (conical intersection-left side of figure 5) and are accessible there can be a fast radiationless decay. ‘Accessible’ means that there is a reaction coordinate with a sufficiently low energy barrier that leads from the initial excited state geometry to the crossing region. In this case, internal conversion can take place within a single vibrational oscillation through, or near, the surface crossing.
(R* → P or R* → R) and radiationless decay occurs on a scale of picoseconds to femtoseconds.

Figure 5. Schematic view of the course of photochemical reaction. There are two possible mechanisms for non-adiabatic radiationless decay: conical intersection where fast radiationless decay occurs on a scale of picoseconds to femtoseconds, and avoided crossing which is much slower than the decay at a surface crossing.

If surface crossings are not present, or are present but are not easily accessible, the process of radiationless decay is better described as the transformation of electronic energy into a manifold of vibronic states associated with the lower electronic state (right side of figure 5). This process is governed by the density of vibrational states and Frank-Condon factor and is much slower than decay at a surface crossing.
I.2. Energy Domain Spectroscopy and Time Domain Spectroscopy

The last two decades of the 20th century have seen a rapid development of ultra-fast laser technology which has provided researchers with shorter laser pulses down to picosecond and even to the sub-femtosecond regimes [21]. Nowadays, a typical femtosecond laser can produce a laser pulse with a duration of <100 fs in the visible region of the spectrum. Femtosecond laser technology has provided us with a powerful tool for the study of molecular quantum dynamics in a real time regime. Before the advent of ultrafast laser technology, energy domain spectroscopy was mostly employed in studying the structure of the electronic, vibrational and rotational structures in molecule [1,2]. Energy domain spectroscopy (EDS) or high resolution spectroscopy is used in order to obtain detailed information on the molecular structure, e.g. the fine and hyperfine structure arising from electron and nuclear spins [1]. EDS has been pushed to the extreme in employing the beautiful properties that a laser provided us, e.g. monochromatic, intense and coherent photons, and our knowledge of molecular structure has been greatly expanded with this technique. By using EDS, we intend to investigate the molecular energy structure as precisely as possible, with the aim of understanding molecular processes and possibly, as one of the ultimate goals to manipulate or control molecules.

Time domain spectroscopy on the femtosecond timescale (or TDS) as a complimentary method to EDS, has provided us with a method to study molecular quantum dynamics by producing ultrashort laser pulses in the femtosecond regime [20-21]. By using ultashort pulses, we approach the problem from the direction opposite to that to EDS, e.g. time resolution is favored instead of energy resolution. From the Heisenberg uncertainty principle:

\[ \Delta E \Delta t \geq \frac{\hbar}{4\pi} \]  

(1.14)

an ultrashort pulse clearly has a broad spectral span in energy, since the time uncertainty \( \Delta t \) is now very small. Hence, the gain from the confinement of time is at the expense of the energy resolution. For example, a 10 fs pulse corresponds to a energy uncertainty of
530 cm\(^{-1}\). As the pulse width is made shorter, the pulse bandwidth subsequently broadens into a wide spectrum of frequencies. Energy domain spectroscopy relies on long pulses, which contain a narrow band of frequencies, and so excite only one or a few states. An ultrashort pulse will excite an ensemble of molecular ro-vibrational levels instead of one single level, which is the goal of EDS. Typically, a femtosecond pulse can excite several molecular ro-vibrational levels simultaneously and coherently. Therefore the coherent superposition of quantum states, often called “wavepackets”, should be considered instead of excitation of a single state. Thus time-resolved molecular dynamics is obtained as a result. As a comparison, EDS makes use of eigenstates in a stationary fashion with no time evolution while fs laser spectroscopy, in a coherent and nonstationary way, uses time evolution as its focus. By creating wavepackets, the uncertainty in the energy of the ultrashort pulse works in favor of the time resolution. The fs pulse provides a spatially well-localized wavepacket, which enables us to observe the vibration and rotation of the molecule in the real time, instead of from the energy spectra.

1.2.1. Generation and detection of vibrational wavepackets

Time-resolved experiments involve the creation and detection of wave packets, defined as a coherent superposition of molecular eigenstates. Due to the differing energy phase factors of the participating eigenstates, this superposition is nonstationary. A typical way to create a vibrational wavepacket is the application of a short \(10^{-12}-10^{-15}\) s (ps or fs) laser pulse to a molecule which is in its equilibrium state. This initial state is often the ground state of the molecule. Thus, the pulse should have a sufficient bandwidth to excite a coherent superposition of the vibrational levels of an excited state, in resonance with the initial ground state at the central frequency of the pulse.
The most widely used scheme for probing the superposition of states of a vibrational wavepacket (i.e. nonstationary state) is the pump-probe experiment. Figure 6 shows the three main aspects of a femtosecond pump-probe wave packet experiment:

1) **The preparation or pump process.** The interaction with a short laser pulse prepares the system under investigation in the nonstationary state. This preparation process sets the zero point of the time scale. The time zero used in obtaining the start of the experiment is defined as the moment when the pump and the probe pulses overlap in time and space at the sample.

2) **The dynamical evolution.** The delay time ($\tau$) is varied so that the signal can be detected as a function of time. Since the intermediate state of the system is nonstationary, one expects a temporal variation of the signal, which is characteristic for the quantum mechanical wave packet motion (here depicted as two distinct wave packets keeping their average energy).

3) **The probing of the nonstationary superposition state.** A second ultrashort pulse interacts with the wave packet typically at a time delay $\tau$. The interaction prepares
the system in a state that can give an experimentally measured signal, e.g. fluorescence, molecular ions or photoelectrons, etc.

1.2.2. Evolution of the wavepacket

A fs laser pulse can coherently excite a set of ro-vibrational states and the wavepacket generated at time $t$ after excitation (after the laser pulse is over) can be written as a time-dependent Schrödinger equation:

$$\psi(t) = \sum C_i e^{\frac{i 2 \pi E_i t}{h}} |i\rangle$$

(1.15)

where $C_i$ is the time dependent transition dipole matrix elements, $E_i$ is the energy eigenvalue of the excited eigenstates $|i\rangle$, $\epsilon_i$ and $\phi_i$ are the amplitude and phase of the laser electric field causing the transition.

Suppose a set of $N$ ro-vibrational levels are coherently excited by the excitation pulse and detected by pump-probe scheme, the time evolution of the wavepacket can be written as:

$$S(t) = S_{\text{const}} + \sum A_{ij} \cos(2\pi \Delta \nu_{ij} t + \varphi_{ij})$$

(1.16)

where the total signal is composed of a constant signal level $S_{\text{const}}$ and a time-dependent part which is a summation over cosine beats, each originating from a single pair of wavepacket’s components $(i,j)$. $A_{ij}$ is the amplitude of each wavepacket component depending on the amplitude of the pulse electric field, $\Delta \nu_{ij}=(E_i-E_j)/h$ is the frequency difference between the ro-vibrational levels $i$ and $j$. $\nu_{ij}$ is the phase difference between various state excitation frequencies; $\phi_{ij}=0$, allowing all excitation occurs simultaneously and coherently.

Equation (1.16) contains the relationship between the wavepacket dynamics and the observed pump-probe signal. It arises from a coherent sum over all two-photon transition amplitudes consistent with the pump and probe laser bandwidths and therefore implicitly contains interferences between degenerate two-photon transitions. It can be
seen that the signal as function of $t$ contains modulations at frequencies $(E_i - E_j)$, the set of level spacing in the superposition (fig. 7).

![Diagram of two pathways leading to the same final state](image)

Figure 7. Two pathways leading to the same final state will give interference (quantum beats) at the frequency difference of the intermediate states (results an oscillatory signal)

### I.3. Outline of the thesis

In this thesis I focus on multi-photon excitation events that result in an electronic transition within a molecule. The thesis is divided into 3 main sections. The first section contains the basic theory on the photo-dissociation/ionization process and details of the experimental apparatus used for the determination of results (Chapters I-II). The second section contains experimental studies of the TDMAE and NO$_2$ molecules on femtosecond timescales (Chapters III–IV). The third section concerns the study of the dissociation of NO$_2$ on nanosecond timescales (Chapter V).

Since photo-excitation, dissociation and ionisation of molecules occurs only in the presence of photolysing light, a broad range of incident wavelengths were used in the experiments described in this thesis. Highly sensitive and selective detection of parent
ions and/or the photo-fragments is achieved when they are mass analyzed. Single photon ionization requires a short-wavelength photon (e.g. VUV) which is difficult to achieve. The advent of lasers made multi-photon ionisation (MPI) possible. If the first of these photons in MPI is in resonance with a particular excited state of a molecule, the efficiency of MPI is enhanced by several orders of magnitude. This results in the ionisation of only those molecules passing through this pre-selected in the intermediate state. The ion imaging technique provides a method for measuring the three-dimensional velocity distribution of both the parent ion and the photo-dissociation products produced during a reaction. The new on-axis ion-imaging apparatus has recently been developed and constructed at the M.L.F. Nijmegen laboratory and based on the design of Eppink and Parker [19].

The next two chapters are experimental studies of the quantum dynamics of two different polyatomic molecules by ultrafast spectroscopy with the implementation of pump-probe techniques, and are grouped together in section two of this thesis. Chapter III presents the study of intermediate electronically excited states, such as Rydberg, Valence, Zwitter Ionic and Charge Transfer, near the first ionisation energy of molecular Tetrakis using the pump-probe detection in conjunction with velocity map imaging technique. By using an ultra-short laser pulse in a two colour laser experiment the detection of short lived intermediate states of this molecule was possible. For this purpose, we ionised the parent molecule and performed a kinetic energy analysis of the ejected electrons. The electrons contain the information about the state that was probed. By varying the time delay between the pump and the probe laser the relaxation of the molecule maybe studied in real time. The imaging method used has an unprecedented efficiency for the observation of the states traversed by the wave-packet created of the initial state. The electronic relaxation gains efficiency by the mediation of the nearby Rydberg states present at this excitation energy. The bulkiness of the molecule allows also the observation of the oscillatory wave-packet movement created on coordinates perpendicular to the relaxation coordinates.

Chapter IV presents the study of dissociative multiphoton ionisation (see section 1.1.4.) of NO₂ by time-resolved velocity map imaging in a femtosecond two-color pump-
probe, 400/600 nm, delay experiment. We observed that most of the ion signal appears as NO$^+$; approximately 600fs period oscillations indicative of wavepacket motion are also observed in NO$^+$ decay. The signal was attributed to a couple of competitive mechanisms. The first two involve three-photon 400 nm absorption followed by dissociative ionisation of the pump state by a subsequent 266 nm photon. The second involves one-photon 400 nm to the $^2\text{B}_2$ state of NO$_2$ followed by two-photon dissociative ionisation at 266 nm.

Finally, the last section of my thesis, Chapter V, presents an experimental study of NO$_2$ using EDS with the dissociated and the resulted products being probed in a (2+1) REMPI process. The photodissociation dynamics (for a general description see section I.1.1) was chosen in the region 200-205 nm to allow the use of a single laser to photodissociate the NO$_2$ molecule and to probe O($^3\text{P}$) and O($^1\text{D}$) fragment channels via (2+1) REMPI technique.

References


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Chapter II

The V.M.I. technique

Ion imaging has emerged over the past few years as powerful means of studying dissociation and ionisation processes. Its clear growth in importance was due to the laser advent for Velocity Map Imaging and also the availability of intense and tunable femtosecond light sources. We have undertaken a series of experiments to study the dynamics of different molecules using supersonic molecular beam in conjunction with velocity map imaging. Imaging is a multiplexing method which provides simultaneous detection of all recoil velocities, both speed and angle, for state selected products. An important advantage of the imaging technique is that all product’s velocities are detected with equal sensitivity, in contrast to the time of flight technique to the time-of-flight technique, which discriminates against low velocities.

II.1. Experimental set-up

The ion imaging apparatus in our laboratory is based on the design of Eppink and Parker [1] fig.1. Since the publication of ref. [1] there have been several improvements in the imaging technique including better inversion methods, particularly the BASEX program, event counting, and direct ‘slicing’ methods that avoid the 2-D to 3-D conversion. In this study we use event counting and BASEX inversion. Although the apparatus is capable of an advanced form of slicing using pulsed delay fields, we found
that the standard ‘crush’ method [1] yielded satisfactory images for all the systems studied in this thesis.

The imaging apparatus consists of a source chamber and the detection chamber separated by a gate valve. The pressure in the source chamber raises from $5 \times 10^{-7}$ to $7 \times 10^{-6}$ torr and the pressure in the detection chamber raises from $2 \times 10^{-7}$ to $3 \times 10^{-6}$ torr, when the pulsed nozzle is turned on with a backing pressure at ~2 bar. The entire system has a volume of 40 l with the source chamber pumped by a 1000 l/s diffusion pump and the detection chamber pumped by a 230 l/s turbo pump.

![Schematic of the imaging experimental set-up.](image)

Fig. 1. Schematic of the imaging experimental set-up. The pulsed valve (PV) is mounted on-axis, $S=2$mm skimmer, the laser focus centered in the ion optics between repeller (R) and extractor (E) electrode, 34 cm TOF tube from the laser focus to detector, dual MCP detector with phosphor screen (PS), CCD camera for spatial detection connected to the PC.

The two chambers are connected via a 2mm skimmer. The skimmer is on axis with the electrostatic lenses. The electrostatic lenses accelerate the charged particles produced by
The V.M.I. Technique

the laser via a 34 cm free electric field TOF tube, to the detector. The purpose of the skimmer is to shape the pulsed molecular beam produced by a solenoid valve from the General Valve Company. Optical access to the detection chamber is provided by 4 CaF$_2$ windows. This allows two laser beams to propagate mutually perpendicular to each other and to the TOF axis between the repeller and extractor of the optic lens assembly. Since the flight tube is vertical, and the detector face is perpendicular to it, a horizontally polarised laser beam has its polarisation axis parallel with the detector face.

After ionisation the charged photofragments are projected along the TOF axis onto a gated dual microchannel plate (MCP) assembly, followed by a phosphor screen. Mass selective selection is achieved by time gating the front MCP with a timed high voltage pulse made by a high voltage switch. A CCD (Fly Pixel) camera records the 2D image on the phosphor screen. This image is recorded in the PC where further data analysis is performed.

The femtosecond apparatus used an off axis molecular geometry which allowed simultaneous TOF-MS and ion imaging. Although the resolution in the off axis case is lower due to velocity spread in the molecular beam, the main resolution limitation for the fs apparatus is due to the short laser pulse ($\Delta t=50$ fs corresponds to 0.04 eV), thus a limiting resolution at 1 eV of 0.04 eV.

II.1.1. The optic lens assembly and detector

Conventional ion imaging techniques utilized grid electrodes to extract and to accelerate ions toward the detector. The disadvantages of grid electrodes are transmission reduction, and image distortions and image blur due to the non-point source geometry. All these problems were solved by the utilization of an open lens electrode assembly. The advance by Eppink and Parker involves simply replacing the conventional grids of the Wiley & McLaren time of flight (TOF) spectrometer with open electrostatic lenses and adjusting the potentials to achieve velocity focusing. These conditions define Velocity Map Imaging in which all products with the same initial velocity vector in the plane parallel to the detector are focused to the same point,
irrespective of their initial distance from the ion lens axis. Under favourable circumstances single ion events at the detector can be detected with an efficiency close to unity. Because of the design of the ion optics the collection efficiency of the photoions is close to 100. The main losses in an ion imaging experiment occur with the visible imaging of the scintillation screen. CCD cameras have a quantum efficiency of between 20% and 30% depending on the wavelength of the phosphor emission. Lens coupling between the screen and the camera chip also introduces losses. These factors mean that one can probably detect about 10% of the product flux. Our system uses a P20 phosphor which although slow (τ~1 ms) has very good emission match to the CCD camera spectral response. By measuring all scattering angles simultaneously, ion imaging has a multiplexing advantage over more traditional time of flight techniques, and this significantly reduces the amount of time required to completely determine a velocity distribution. One disadvantage of Velocity Map Imaging is that the 1:1 position: velocity correlation of ion imaging is changed by a magnification factor N. The apparatus must be calibrated for this factor (see section II.2)

II.1.2. The lasers

Two types of experiments were carried out using nanosecond or femtosecond lasers. The nanosecond experiment was performed with a dye laser at 10 Hz repetition rate and a frequency tripling unit. The dye laser (Narrow Scan) was pumped with 532 nm radiation of a Nd:Yag laser and the main output is ~600 nm (figure 3). The fundamental wavelength was frequency tripled using a first KDP crystal for doubling and then a BBO crystal for tripling. After dissociation, the fragment velocity causes a Doppler shift the REMPI transition, so the probe laser have to be scanned over the Doppler width in order to ensure equal detection efficiency to all fragments.
The doubled and the tripled frequencies were separated by a Pellin-Broca prism so the doubled frequency could be blocked. Using a $\lambda/2$ wave plate the laser polarisation was flipped to horizontal polarisation. This light, ~1mJ/5ns, was then focussed into the ion imaging apparatus with a 15 cm lens and had two roles: to dissociate the molecule and to detect atoms in a certain quantum state via a (2+1) REMPI process (see chapter V).

The femtosecond experiment was performed with a Titanium Sapphire laser. The fundamental wavelength of the laser is 800 nm with a repetition rate 20Hz. In order to perform a pump-probe experiment the main output of the laser was split in two laser beams (figure 4). The pump laser beam was a 266 nm obtained by frequency tripling of 800 nm. The probe laser beam is obtained by doubling of 800 nm in a KDP crystal and the resulting 400 nm light passes a delay line made specially to vary the time delay.
between the pump and the probe laser beams. Both laser beams are focused (lens: \( f=50 \text{ cm} \)) and collinearly combined into the ion imaging apparatus.

**Fig. 4.** Schematic of the femtosecond pump-probe laser. The pump laser beam was a 266 nm obtained by frequency triplet of 800 nm. The probe laser beam is a doublet of 800 nm.

### II.2. VMI and data analysis

Figure 5 shows a schematic of how the velocity of a charged particle can be imaged using a detector-CCD assembly. A molecular beam is pointed along the TOF detector axis and crossed with the laser beams. The polarisation of the dissociation light is parallel to the detector plane and perpendicular to the TOF axis. As described in section I.3, chapter I, the polarisation light direction defines the velocity vector of the fragment.
The charged particles (ions or photoelectrons) are created by the laser in the crossing area and are emitted with an energy $E_{KER}$. The electrostatic lens produces an electric field and repels charged particles into the Time of Flight (TOF) tube where heavier particles will arrive later at the detector. This effect is used to measure mass selectively by turning the detector on at the right time as a certain mass arrives.

The charged particle form in space a sphere that evolves along the TOF axis and subsequently crushes onto detector resulting a 2D image with radius $R_{\text{max}} = v_\parallel \Delta t / N$. The filling pattern reveals the angular distribution.

However, this transform can lead to a reconstructed image that are very noisy and contain singularities due to the form of the transform integral. Reisler and co-workers [6] developed the basis set expansion (BASEX) method to produce much higher quality reconstruction. This method expands the 2D image projection in a basis set of well-behaved, Gaussian-like functions. The full 3D distribution is then reconstructed as a
linear combination of these Gaussian-like functions. A slice through this 3D distribution is presented in a 2D as an “inverted image” from which the speed spectrum and angular distribution is extracted.

Let $L$ be the distance between the acceleration region and detector and $\Delta t$ the time for the particles to travel this distance (figure 5). The velocity along the symmetry axis is given by equation: $v_\perp = \frac{L}{\Delta t}$. The velocity of the particle parallel to the detector is: $v_\parallel = N\frac{R_{\text{max}}}{\Delta t}$, where $N$ is the magnification factor which depends on ratio $f = \frac{V_E}{V_R}$ (voltage on the optic lens) and usually lies between 1 and 1.4. Because the magnification factor varies as a function of distance from the repeller plate, a calibration image of the same mass is usually taken.

The photoelectrons formed from photoionization are susceptible to the Earth’s magnetic field along with other stray magnetic fields. Due to this fact the electron images are often slightly distorted (are not round). To improve this, the electron optic and fly tube assembly can be enclosed with magnetic shielding, which is in generally μ-metal (Magnetic Shielding Corp.) The image can also be improved by carefully positioning a magnet in the vicinity of the detection unit.

References


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Chapter III

Femtosecond time resolved photoelectron imaging study of electronic relaxation in the tetrakis molecule

Abstract

Femtosecond time resolved photoelectron imaging in conjunction with the pump probe technique has been applied to the electronic relaxation of an ethylene-like molecule, tetrakis dimethyl aminoethylene, excited to ππ* a valence state. This method has an unprecedented efficiency for the observation of the states traversed by the wavepacket created in the initial state. The existence of a mediating state for the ultrafast electronic relaxation in this ethylenic-like molecule has been revealed. This state is of Rydberg character and its high efficiency is due to its ability to link the electron distribution of the initial and final electronic states. This mechanism yields a longer time evolution compared to the coupling through conical intersection that is invoked usually to rationalize ultrafast decay.
Chapter III

III.1. Introduction

The Born-Oppenheimer approximation, which assumes an adiabatic separation of electronic motion from nuclear motion, has a pivotal role in defining the potential energy surface of a molecule and thus permits a mechanistic picture of molecular dynamics. Minima on the potential energy surface for the nuclei can be identified with the classical picture of equilibrium structures of molecules. The breakdown of the Born-Oppenheimer approximation is due to the motion of the atoms near the “intersections of potential surfaces belonging to a different electronic state, called a conical intersection” [1] (see fig. 2). These have been abundantly found in triatomic molecules as well as in polyatomic ones [2,10]. Ultrafast experiments, such as reported in [3] are readily interpreted in terms of conical intersections.

Molecules rarely reemit from the initially excited level after the absorption of a photon and if the molecule is sufficiently complex, light emission, a slow process, is not the main decay channel for the excited state. The relaxation process, rapid in general, is essential to maintaining life since DNA molecule is continuously exposed to light and photochemistry can be harmful to it [4]. The energy is rapidly dissipated among the atoms of the molecules preventing the bonds braking. These properties arise from the coupling between the electronic configurations (non adiabatic couplings) of the molecular systems accessible by optical excitation, and the other energetically accessible configurations. The crossing between potential surfaces, named conical intersection, allows extremely fast relaxation in molecules. This intersection connects directly the relevant excited state. The process provides a descent to the lowest energy surface guided by the gradients along these surfaces. However, recent discussions [5] show that the passage by a conical intersection where the non-adiabatic coupling is not fully fulfilled (the surfaces are close but not crossed) has the effect of increasing the relaxation time. In such case, the relaxation mechanisms can become slow as compared to molecular movements. Typically in ethylene-like compounds was shown [6-9, 9, 10] that besides the direct connection of the initial and final potential energy through a
conical intersection, a complementary, general mechanism exists and increases the relaxation rate.

We propose here that such a mechanism exists and involves mediating states or surfaces allowing a more direct connection between the relevant excited surfaces. We have identified these states in the case of a specifically selected ethylenic-like molecule tetrakis dimethyl amino ethylene (TDMAE).

![TDMAE molecule](Image)

**FIGURE 1.** The TDMAE molecule.  
**FIGURE 2.** Schematic of the $V(\pi\pi^*)$-$Z$ surface crossing in TDMAE.

Ethylene has been recognized as exhibiting a conical intersection between the Valence ($\pi\pi^*$ of $C^*-C^*$ bi-radical type) state and a Zwitterionic state ($Z$, $C^+-C^-$) [11,12], these configurations were early recognized as accidentally degenerated in energy [13]. The later $Z$, intersects with the ground state $N$ and achieves the dissipation of the electronic energy. The $V$-$Z$ coupling is caused by the different symmetry $^1B_{1u}$ and $^1A_g$ respectively. The active coordinates for this conical intersection are composed by C-C torsion coordinate. Has been shown by Martinez et al. [14] that in the vicinity of the crossing the population decay is longer than 100fs although the deformation of ethylene only requires the displacement of the very light H atoms. Our claim in the present study
is that a mediating Rydberg state may help to link the crossing states in Tetrakis molecule since the group to be displaced is very heavy. More recently the non-adiabatic coupling of the 3s Rydberg-V state has also been proposed [15]. This question of Rydberg participation may appear as controversial in ethylene, but expectedly not in heavier ethylenic compounds. Therefore, experimental observations are necessary in order to certify Rydberg-Valence interaction. Generally, in ethylene-like molecules both Valence and Zwitterionic states are relatively high in energy with respect to the ionization potential and overlap well with Rydberg states (see fig.3).

We show here, on a specific example, evidence for a direct descent from the Valence to a Rydberg surface(s), followed by evolution towards the Zwitterionic state.

TDMAE has been excited by a femtosecond laser (pump) in the UV at 266 nm and the relaxation has been followed by a second femtosecond laser (probe) that probes the evolution by photoelectron spectroscopy. The probe laser ionises the TDMAE molecule and the resulting photoelectron spectrum is a fingerprint of the evolution of its electronic configuration [6, 11]. For each traversed electronic state there will be a different electronic spectrum indicative of the energy of the electronic state and its nature: Valence, Rydberg or Zwitterionic.

III.2. Experimental set-up

The time resolved photoelectron spectra have been recorded in a special spectrometer with high collection efficiency: an ion velocity imaging device based on the design of Eppink and Parker [16], used here for electrons. The molecular beam in the Saclay apparatus is off-axis to the electrostatic optics. Perpendicular extraction has the advantage of allowing easy visualisation of the molecular beam translational cooling and hence its optimisation. On axis to the detector face a Wiley-McLaren time-of-flight mass spectrometer (TOF) allows one to survey the spectra of the various photofragments. The ionisation process creates an expanding sphere of electrons which is projected on a sensitive pair of micro-channel plates (MCP’s) in which mass resolution is achieved by gating the voltage applied to the front MCP. The emitted electrons excite a phosphor
screen and the image is captured by a CCD camera (LaVision) resulting a 2D image. The 2D images are created and averaged using the DaVis software package (LaVision) and stored after accumulation at each delay step. The raw images (2D) are inverted by the Henkel method or by simulation using a sum of Gaussians [17]. Electrons of increasing kinetic energies correspond to spheres of increasing sizes.

The ion imaging set-up is coupled to the LUCA femtosecond laser facility of Saclay. This is a Titanium-Sapphire regenerative amplifier centered at 800 nm and operated at 20 Hz repetition rate. For these experiments, the pump and probe pulses at 226 nm and 400 or 800 nm, respectively, are generated by frequency mixing. The main output, 800 nm, of the laser is split in two beams after recompression, yielding a 58 fs pulse length. The beam splitter is accomplished by a titled window, the coupling being polarisation sensitive. Thus the intensity ratio between both pump and probe beams can be varied by the rotation of a half wave plate. The pump beam is used directly after the frequency doubling while the probe beam is delayed by an optical delay line. The two beams, pump and probe, are recombined in the vacuum chamber at a small angle and are independently focused onto the molecular beam in about 200 μm diameter spot by the thin lenses outside the chamber. The pulse energies that are injected onto the machine are up to 200 μJ at 800 nm, 100 μJ at 400 nm and 70 μJ at 266 nm. The pump and probe beam polarisation are generally set parallel to each other and they are also parallel to the detector face. Room temperature tetrakis was seeded in helium and expanded in vacuum through pulsed nozzle into a skimmed molecular beam chamber. The skimmed molecular beam was intersected at 90° with the pump (266 nm) and probe laser (400 nm or 800 nm) beams. The pulsed nozzle is a General valve with 0.3 mm in diameter and an opening time of 160 μs. The backing pressure was maintained at 1.5×10⁻³ torr.

An experiment with an effusive beam (room temperature experiment) was also performed, by introducing pure TDMAE through a needle valve inside the detection region under an operating pressure of 10⁻⁵ torr. This arrangement is useful in checking our data for the clusters influence; room temperature TDMAE is indeed free of clusters.
III.3. Ultrafast decay

The mechanism of the electronic relaxation in TDMAE is similar with ethylene (C\textsubscript{2}H\textsubscript{4}). It was shown by Mulder et al. [18], that a conical intersection is expected in any photochemical reaction in which a double bond is twisted.

![Schematic view of a course of a photochemical reaction](image)

FIGURE 3. Schematic view of a course of a photochemical reaction. The pump laser brings the molecule on the valence state surface after ~300fs, via a non-radiative decay process, the wave packet moves to the zwitterionic state passing a conical intersection V-Z. The two surfaces exchange their character in this region, hence having steep slopes that strongly affect the planarity of the central skeleton. The CC bond is abruptly twisted which subsequently alters the position of the adjacent N atoms.

The various mechanisms of the electronic relaxation of TDMAE have been previously reported by Soep et al. [19]. They described the relaxation pathways in terms of generic properties in the excited states of double bond molecules exemplified by ethylene, from the very initial step in the Frank-Condon zone, down to a fluorescent state, over widely different time scales ranging from femtosecond to nanosecond.
Time resolved observation of multiple electronic timescales, as observed by ion and fluorescence detection (see fig. 3). With a femtosecond pump at 266 nm (4.6 eV), a wavepacket is formed that initiates a rapid downhill movement along the slopes of the excited potential energy surface. Initially, the wavepacket prepares a near planar geometry of the molecule with a valence configuration $\pi\pi^*$ or $\text{C}^*\cdot\text{C}^*$ which evolves to a state assigned with a zwitterionic character $Z$ ($\text{C}^+\cdot\text{C}^-$). Subsequent relaxation with a 120 ps time constant occurs to a charge transfer state CT. This latter state has the positive charge delocalised on the dimethylamino groups. This decay was observed through ion detection at the mass of TDMAE$^+$.  

**III.4. Time resolved photoelectron spectra**

Time resolved photoelectron spectroscopy (TRPES) has been proposed as a useful technique for the study of ultrafast non-adiabatic processes in isolated polyatomic molecules. TRPES is able to reveal the nuclear dynamics involved in coupled electronic states of polyatomic molecules. The photoelectrons kinetic energy spectra in a non-adiabatic coupling leads to a changing electronic state symmetry characterised by a rapid shift of electrons from an energetic band to a low energy band.

The ion velocity imaging technique is perfectly adapted to femtosecond time dependent photoelectron spectroscopy due to its very high sensitivity, where the electron counting rate is very similar to that of the corresponding ion [20]. The energy resolution of the device is fully compatible with the frequency spread of 50 fs Gaussian pulses, and in addition the technique yields another dimension, the angular distribution of the electrons with respect to the ionising laser field. This information concerning the angular distribution of the ejected electrons, although complex since it depends upon many parameters, can essentially describe the evolution of the excited system through different electronic configurations.

Figure 4 shows the spectrum which is obtained through the radial integration of the images for various time delays between the 266 nm pump and 800 nm probe, with a typical image being shown in the right insert of figure 4. Here, four groups of bands can
be seen, only one of which is weak (A’) and is magnified on top of the figure. The first peak, denoted as peak A, close to the zero of energy of the electrons, with shoulders extending to 0.6 eV. The cumulated energy of the pump and probe lasers is 6.2 eV, which allows disposal of a maximum 0.8 eV for the electrons with the 5.4 eV ionisation potential of TDMAE. Therefore any band beyond of the A shoulders will involve a two photon ionisation which is attainable with the probe laser intensity of ~100 μJ. The single photon character of band A is verified by using a 400 nm probe, twice of energy of 800 nm. The figure 5 shows bands B and C together with bands A’; band A is more intense due to an one photon excitation and is located at ~1.6 eV (0.1eV+1.55eV). These bands exhibit different time evolutions: peak A exhibits an exponentially decays in 200 fs convoluted by cross correlation time of the laser. The band A ends onto a small plateau (5%).

FIGURE 4. Radially integrated electron velocity images of TDMAE excited at 266 nm and ionized at 800 nm. Each curve corresponds to a pump/probe time delay. The top insert is a magnification of bands A’ and B. The insert on the right is the complete electron velocity image, but time integrated.
Peak B rises in 200 fs corresponding to the decay of A as is clearly apparent at 1 eV in figure 4 and 5 where the band B is retarded with respect to the band A. The decay of peak B is 380 fs and is accompanied by the equivalent rise of peak C in 380 fs.

The additional peak A' seen at 1.6 eV mimics the evolution of the peak A. This is also verified in figure 5 where A' formed by 400 nm photon is more intense as induced by two 800 nm photon. The figure 5 displays the same sequential scheme as figure 4: band A' appears first at 1.6 eV, decays into B which in turn forms C. Measurements have been taken at longer times delay for the 266/800 nm scheme and reveal that band C can be identified with the long lived state, 100 ps lifetime, assigned to the Z state [21].

The sequential decay which is apparent here, through the observation of band B, reveals the existence of a new transient not detected so far by the observation of TDMAE⁺. This intermediate state is difficult to assess in ethylene, if existing. In case of TDMAE, the bulkiness of the molecule and the inertia of the moving groups slow down

![Figure 5](image_url)
all the movements. In TDMAE, instead of H atom, \( \text{N(} \text{CH}_3)_2 \) groups with a mass ratio of 44 are moved. We suspect (see below) that this state can belong to a Rydberg series converging to the adiabatic ionisation potential at 5.4 eV. The assignment of the bands A, B and C to different electronic states (configurations) is further supported by polarisation measurements, where the angular distribution of the electrons with respect to the ionisation laser is recorded as displayed in figure 6.

The polarization parameters \( \beta \) extracted from images data represent the degree of the alignment of the ejected electrons with respect to the probe ionization laser polarization direction. The anisotropy \( \beta \) is obtained by a simple fitting of the angular dependence to the second order of the expansion \( I(\theta) = (1/4\pi) [1 + \beta P_2 \cos \theta] \), where \( P_2 \) is a second order Legendre polynomial [22]. This is an approximation given by two photon ionization process of the transient state and justified by a good agreement between the simulated angular distribution with \( \beta_2 \) and the experimental results.

![Figure 6](image-url)
From figure 6 we can see that beyond the 100 fs delay the anisotropies associated with bands B and C show values clearly constant, $\beta=1.5$ and 0.9 respectively during the life time of the observed transient species.

The high polarization observed for B is compatible with a Rydberg state assignment. A maximum value $\beta=2$ can be obtained in a single photon ionization of an atom if an s orbital is ionized. Molecular Rydberg states retain a strong asymptotic atomic character, thus the anisotropy of the ejected electron originated from the Rydberg orbital remains high [23]. The low lying Rydberg states are strongly influenced by the molecular core. This produces a mixing of the partial electron waves making the assignment of the ionized state via angular distribution difficult [24]. The C band that was assigned to a Zwitterionic state also keeps a diffuse character that may explain its anisotropy. However, it is difficult to assess by anisotropy measurements the nature of A state.

### III.5. Oscillatory wavepacket motion

Presently we have reported on the time evolution of the excited TDMAE molecule, as implicitly consisting of a damped motion, where the wavepacket created on the Valence $\pi\pi^*$ surface could be rapidly spread over the several coordinates of the potential surface after passage of the conical intersections. This spreading should result from the C-C twist and the pyramiding of carbon 1 (figure 1and 2). The oscillations describe the persistence of the coherence during the relaxation of the system and characterised vibrational movements of the evolving system. Figures 4-5 reveal an apparently different situation where peak C shows important modulations with a 500 fs period that increases in amplitude as time goes by. Cuts of these bands have been made for bands B and C in figure 7. They are well simulated using simple exponential evolution and oscillatory behaviours. It is clearly evident that the oscillations increase within the 1200 fs time domain and this is independent from the decay of the B and C bands. These oscillations are in phase in B and C as shown in figure 7.
Chapter III

FIGURE 7. Left, time evolution of peaks B and C. Right: oscillatory part of these evolutions after subtraction of the exponential rises and decays

We hence infer that the observed vibrational coherence corresponds to a movement on a different coordinate than the ‘reaction coordinate’ [25,26]. In the case corresponding to the reactive coordinate it would be rapidly damped after the rise of the band B. The oscillatory movements for TDMAE occur on a perpendicular coordinate to the evolution of the decay. The full analysis of these wavepacket movements will be subject of a forthcoming paper.

III.6. Conclusions

Photoelectron imaging has revealed the existence of a short lived (380 fs) intermediate state in the relaxation pathway of Valence (\(\pi\pi^*\)) excited TDMAE. This state is traversed by the wavepacket descending from the excited region. It has been assigned to a Rydberg configuration and should be a key transient in the electronic relaxation mechanism of the ethylene like molecules. The Rydberg intermediate provides in the molecule that we have studied, TDMAE (Tetrakis) with sufficient electron density to accomplish the electron transfer to a Zwitterionic configuration. The relaxation mechanism that is was propped here is fairly general and should be apply to many conjugated organic molecules of low ionization potential. The relaxation of the electronically excited states should often be facilitated by the passage through surfaces of diffuse electronic configuration as Rydberg character.
Time resolved observation of multiple electronic...
Chapter III

Chapter IV

Dissociative multiphoton ionization of NO$_2$ studied by time-resolved imaging

Abstract

We have studied dissociative multiphoton ionization of NO$_2$ by time-resolved velocity map imaging in a two-color pump-probe experiment using the 400 and 266 nm harmonics of a regeneratively amplified titanium-sapphire laser. We observe that most of the ion signal appears as NO$^+$ with ~0.26 eV peak kinetic energy. Approximately 600 fs period oscillations indicative of wave packet motion are also observed in the NO$^+$ decay. We attribute the signal to two competitive mechanisms. The first involving three-photon 400 nm absorption followed by dissociative ionization of the pumped state by a subsequent 266 nm photon. Multiphoton Dissociation of the NO$_2$ molecule by three-photon 400nm absorption and followed by one photon 266nm is the second mechanism. The third mechanism involves one-photon 400 nm absorption to the $^2B_2$ state of NO$_2$ followed by two-photon dissociative ionization at 266 nm. This interpretation is derived from the observation that the total NO$^+$ ion signal exhibits biexponential decay, $0.72 \exp(-t/90\pm10) + 0.26 \exp(-t/4000\pm400)$, where $t$ is the 266 nm delay in femtoseconds. The fast decay of the majority of NO$^+$ signal suggest a direct dissociation via the bending mode of the pump state.
IV.1. Introduction

Femtosecond time-resolved imaging spectroscopy is emerging as a practical and versatile technique with which to study nonadiabatic processes in polyatomic molecules [1]. The time-resolved photoelectron kinetic energy spectrum [2] and its concomitant angular distribution [3] are sensitive probes of internal conversion [4], vibrationally mediated spin-orbit coupling (intersystem crossing) [5], intracluster reaction dynamics [6,7], dissociative ionization [8], reaction mechanism [9], and other non Born-Oppenheimer dynamics [10]. Measurements of the time evolution of the photoion signal are in general less sensitive to the details of the electronic dynamics because the photoionization cross section is not so affected by vibronic coupling as the energy of the ejected electron, but nonetheless important information can be gleaned from such measurements [11].

For many years, NO$_2$ has served as a benchmark polyatomic molecule for studies of unimolecular reaction dynamics, intramolecular vibrational redistribution, and vibronic coupling because of its rich and complex behavior despite its apparent simplicity as a triatomic molecule. There is an extensive literature, too vast to review here, concerning frequency domain studies of the dynamics of NO$_2$. Developments in short pulse lasers have also prompted a number of groups to revisit the dynamics of this intriguing molecule in the time domain in recent years. In particular, Wittig and co-workers [12,13,14] and Tröe and co-workers [15,16] have measured the energy dependence of the unimolecular rate coefficients close to the dissociation threshold. These measurements are a sensitive test of statistical theories which predict a microcanonical unimolecular rate constant given by

$$k(E) = \frac{N^+(E-E_0)}{\hbar \rho(E)}$$

(1.1)

where $E_0$ is the reaction threshold, $N^+(E-E_0)$ is the number of open channels at the transition state, and $\rho(E)$ is the density of coupled molecular states at the energy $E$. 

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Of course, time resolution comes at the expense of energy resolution. Wittig and co-workers employed pump-probe photofragment excitation (PHOFEX) spectroscopy, in which they monitored the appearance of the NO product by laser induced fluorescence (LIF). In other experiments using a femtosecond laser Ionov et al. [12] were able to measure $k(E)$ up to about 800 cm$^{-1}$ of excess energy where the rate is $1.3 \times 10^{12}$ s$^{-1}$ but at the cost of energy resolution (40–70 cm$^{-1}$).

Fig. 1. The four lowest lying electronic states of NO$_2$ are strongly coupled by vibronic interactions. The pairs of states labeled $^2A_1$, $^2B_1$, and $^2A_2$, $^2B_2$ are components of a Renner-Teller pair correlating to $^2\Pi_u$ and $^2\Gamma_g$ states in linear geometry. In the near UV the dominant absorption occurs for transitions from the $^2A_1$ ground state to the $^2B_2$ state. For wavelengths below 397.9 nm this leads to dissociation on the ground state surface via the path indicated in the figure in which the excited molecule initially relaxes towards the minimum of the $^2B_2$ state, inducing motion that tightens the bond angle. At a bond angle of about 114° the $^2B_2$ adiabat crosses through the ground state. Close to this point the Born-Oppenheimer approximation is not valid and the electronic character of the excited state is mixed with that of the ground state. A wave packet created by a short pump pulse can then cross to the $^2A_1$ state where it continues to evolve along the O-NO stretching coordinate, eventually leading to dissociation into NO($X^2\Pi$) and O($^3P$).
Troë and co-workers adopted a slightly different approach and observed the depletion of the dissociating NO$_2$ by monitoring the LIF signal from the $1\ ^2\Pi_u(3d)$ and $1\ ^2\Sigma_u^+(3p)$ Rydberg states in a femtosecond pump-probe experiment. By varying the temperature of the sample but keeping the photolysis wavelength fixed the effect of rotational excitation on the decay rate, $k(E,J)$, was also measured in these experiments.

The results of both the Wittig and Troë groups are in broad agreement and both are consistent with the predictions from statistical unimolecular rate theory. However, structure is apparent in the detailed energy dependence of $k(E,J)$ and on a microscopic level the dissociation appears to be governed by specific resonance states whose widths show fluctuations around average values which are related to the specific rate constants from statistical theories [17].

The complexity observed in the detailed energy dependence of the unimolecular rate constants is manifest in the near UV absorption spectrum of NO$_2$ both above and below the first dissociation threshold [18] of 25128.57±0.05 cm$^{-1}$ and is due to the vibronic coupling between the four lowest electronic states of molecule (see Fig. 1). Around this excitation energy the absorption cross section is dominated by transitions from the $\tilde{X}\ ^2A_1$ ground state to the $\tilde{A}\ ^2B_2$ state with little contribution to the $\tilde{B}\ ^2B_1$ or $\tilde{C}\ ^2A_2$ states. However, the $\tilde{A}\ ^2B_2$ state is embedded within the $\tilde{X}\ ^2A_1$ electronic ground state and is strongly coupled to it due to a conical intersection between the two potential energy surfaces (PESs). Excitation above the conical intersection therefore leads to rapid internal conversion and an extremely complicated absorption spectrum [19].

The nuclear dynamics leading to dissociation is now generally agreed to involve a decrease in bending angle as the molecule moves from the Franck-Condon region of the $\tilde{A}\ ^2B_2$ state immediately accessed by the photolysis photon towards the conical intersection with the $\tilde{X}\ ^2A_1$ state. Once the electronic character reverts to the $\tilde{X}\ ^2A_1$ state the nuclear dynamics follow a stretching motion along the O-NO coordinate. Support for this model comes from ab initio calculations. One such recent calculation [20] locates the $\tilde{X}\ ^2A_1/\tilde{A}\ ^2B_2$ conical intersection at $R = 131.1$ pm and $\alpha = 113.6^\circ$ at an energy $T_e = 1.210$ eV above the ground state minimum ($R = 118.7$ pm and $\alpha = 133.8^\circ$) [21]. This model is also supported by observations of the NO product state and angular
Dissociative multiphoton ionization of NO$_2$... distributions as observed by ion imaging [22] or velocity mapping [23], for example, and in the time domain by the photoelectron-photoion coincidence imaging experiments of Davies et al. [24,25].

Importantly for the discussion that follows, the experiments of Davies et al., which were carried out at a single wavelength of 375 nm for both pump and probe pulses (width 100 fs, intensity $\sim 10^{12}$ W cm$^{-2}$), identified a dissociative multiphoton ionization (DMI) pathway due to a three-photon excitation of NO$_2$ to a repulsive potential correlating with NO(C $^2\Pi$) + O($^3P$) followed by single-photon ionization of NO to form $^1\Sigma^+$ ground state NO$^+$. This finding was not in accord with earlier work of Singhal et al. [26] who had investigated the multiphoton ionization and dissociation pathways of NO$_2$ in a single pulse. These experiments also employed 375 nm light but with shorter 50 fs pulses and an estimated intensity of up to $5 \times 10^{13}$ W cm$^{-2}$, and had concluded that the observed NO$^+$ signal was due to one-photon excitation of the $^2A^2_2$ state of NO$_2$ followed by electronic predissociation on the ground state PES and subsequent three-photon ionization of NO(X $^2\Pi$). Some signal from N$^+$ and O$^+$ was also observed and attributed to dissociation of the NO molecule.

In order to investigate the effects of laser field intensity on the multiphoton dissociation dynamics of NO$_2$ in more detail López-Martens, Schmidt, and Roberts [30] employed two-color fluorescence depletion spectroscopy using a 400 nm pump and 800 nm probe. Dissociative production of NO in the $^2A^2\Sigma^+$ state was monitored through the depletion of the $^2A^2\Sigma^+ \rightarrow ^2X^2\Pi$ fluorescence induced by the 800 nm probe. For 400 nm pump intensities between $3 \times 10^{12}$ and $2 \times 10^{13}$ W cm$^{-2}$ these authors concluded that the dominant dissociation pathway involved three-photon absorption of 400 nm light to a highly excited state of NO$_2$ (situated $\sim 9.3$ eV above the ground state minimum). This state was estimated to dissociate to NO($^2A^2\Sigma^+, \nu = 0, 1, \text{and } 2$) + O($^3P$) on a time scale no longer than 600 fs. Thus the primary dissociation mechanism is similar to that proposed by Davies et al [24] although a different intermediate electronic state of NO$_2$ must be involved since three-photon 400 nm excitation has insufficient energy to reach the NO(C $^2\Pi$) + O($^3P$) asymptote even in a room temperature sample of NO$_2$. 

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In this paper we report our first attempts to follow the dynamics of the internal conversion and the subsequent dissociation of an optically prepared sample of NO₂ in the $\tilde{A}^2\text{B}_2$ state as it crosses over to the ground $\tilde{X}^2\text{A}_1$ state by time-resolved imaging of both photoelectrons and photoions. The idea behind our experiment is that as the electronic configuration changes from $\ldots \{(5a_1)^2(1a_2)^2(4b_2)^2(6a_1)^2\}$ to $\ldots \{(5a_1)^2(4a_2)^2(6b_2)^2(6a_1)^1\}$ we expect to be able to detect a change in the photoelectron kinetic energy release spectrum (and its angular distribution). Concomitant changes are also to be expected in the time-resolved photoion yield spectrum as the nuclear dynamics cause the molecule to sample different Franck-Condon windows to the cation.

The paper is organized as follows: in section IV.2 we describe specific features of the Saclay Laser-Matter Interactions Center (SLIC) laser facility and the general experimental arrangement. Section IV.3 describes the observations. The key observations are a sub 100 fs rise time followed by a longer lived oscillatory decay in the NO⁺ signal as a function of the 266 nm delay, and that the NO⁺ ions are observed with significant translational energy. These results are interpreted in Sec. IV.4 in terms of a DMI mechanism that is similar to that previously proposed by López-Martens et al., [27] but which may also be sensitive to the internal conversion dynamics between the $\tilde{X}^2\text{A}_1/\tilde{A}^2\text{B}_2$ states of NO₂. Finally we draw together our conclusions in Sec. IV.5.

IV.2. Experiment

The experimental apparatus used for the real time experiments reported here associates a pulsed supersonic beam with an ion/electron imaging device. It is coupled to the SLIC femtosecond laser facility. The master laser is a titanium-sapphire regenerative amplifier centered at 800 nm and operated at 20 Hz repetition rate. For our experiments, the pump and probe pulses at 400 and 266 nm, respectively, are generated by frequency mixing. The 800 nm output is split into two beams after recompression, yielding a 40 fs pulse (full width at half maximum). Beam splitting is accomplished by a tilted window, the coupling being polarization sensitive. Thus the intensity ratio between both pump
Dissociative multiphoton ionization of NO₂...

and probe beams can be varied continuously by the rotation of a half wave plate. The pump beam is used directly after frequency doubling whilst the other beam isdelayed before third harmonic generation, by an optical delay line. The two beams, pump and probe, are recombined in the vacuum chamber at a small angle and independently focused onto the molecular beam by thin lenses outside the chamber. The cross correlation width of the laser pulses is of the order of 90 fs as measured by nonresonant three-photon ionization of NO diluted in He. The pulse energies that are injected into the machine are up to 100 μJ at 400 nm and 70 μJ at 266 nm, but typically 10–15 μJ at 400 nm and 5–15 μJ at 266 were used. They are focused to a 200 μm diameter spot yielding a typical intensity of 5×10¹¹ W cm⁻². The pump and probe beam polarization are generally set parallel and they are also parallel to the imaging plane.

The supersonic beam has already been described in a previous paper [28]. For the current experiments a 2% NO₂/5% O₂/helium gas mixture was expanded through a pulsed nozzle, 300 μm in diameter. O₂ was added to the gas mixture in order to displace the NO₂/NO equilibrium towards NO₂. The backing pressure was maintained at a relatively low value of 1.2 bar in order to minimize the production of N₂O₄ and higher clusters. However, from the known equilibrium constant (0.15) for N₂O₄ ⇌ 2NO₂ at 25°C the N₂O₄ concentration still comprises 50% of the sample. This does not affect measurements with the 400 nm pump since the absorption of NO₂ dominates at this wavelength. The opposite is true at 266 nm where N₂O₄ absorbs weakly, while NO₂ is transparent.

A velocity map ion/electron imaging device based on the design of Eppink and Parker [28] has been used. The electrostatic optics are arranged in our apparatus to image perpendicular to the molecular beam. This configuration does not give the best resolution for the angular distributions of the ion images [30] owing to the velocity spread in the supersonic beam. However, the major contribution to the spread in velocity distributions arises from the femtosecond excitation with ca. 40 meV width. Perpendicular extraction has the advantage of allowing easy visualization of the molecular beam translational cooling and hence its optimization. The perpendicular configuration has also been chosen to allow a Wiley-McLaren time-of-flight mass (TOF)
spectrometer to be placed opposite the imager. The TOF allows convenient optimization of the pump-probe conditions and survey spectra of the various photoions. Since the electric fields in a velocity map imaging spectrometer can be adjusted to magnify the velocity map to practically any size, the pixel-to-velocity calibration factor for any given set of focusing voltages of the spectrometer needs to be measured [31]. For this purpose, we use photoelectron images from xenon at $10^{-6}$ Torr obtained by three-photon 266 nm ionization. This results in Xe$^+$ $^2P_{3/2}$ and $^2P_{1/2}$ ions with an energy separation of 1.31 eV. The images from the microchannel plate (MCP)/phosphor detector are collected in time step multiples of 0.67 fs using a charge-coupled device camera (LaVision), in which mass resolution is achieved by gating the voltage applied to the MCPs. The images are stored and processed (e.g., averaged) using the DaVis software package (LaVision) at each delay step. Each raw image is then inverted by the Hankel method or by simulation using a sum of Gaussians [32].

IV.3. Results

The pump-probe scheme of the present experiments is illustrated in Fig. 2. The pump pulse, centered at ~400 nm, excites jet-cooled molecules initially in the lowest vibrational and rotational levels of the $X^2A_1$ state to zero-order rovibrational levels of the $\tilde{A}^2B_2$ state. The population in the $\tilde{A}^2B_2$ state can be probed by two-photon ionization through a number of Rydberg states [1 $^2\Sigma_u^+(3p)$ is illustrated] converging to the $X^1\Sigma_g^+$ state of NO$_2^+$ or as in the experiments of Abel et al. [33] by monitoring the fluorescence from these intermediate states. In our experiments, we detect NO$^+$ and NO$_2^+$ as a function of the pump-probe delay.

Because of the linear momentum conservation of the nuclei upon ionization, the relatively low lying zero-order vibrational levels of the $\tilde{A}^2B_2$ state will preferentially prepare equally low lying vibrational levels of the ground electronic state of the cation ($^1\Sigma_g^+$) with near maximal available kinetic energy to the photoelectron, whereas the
reverse will be true for the relatively high lying vibrational states of the \( \tilde{X} \) \(^2\)\(A_1\) state, the time evolution of the photoelectron kinetic energy release (KER) spectrum thus provides a potentially sensitive probe of the internal conversion dynamics.

Fig. 2. The pump-probe schemes adopted by Troe and co-workers (Ref. 33) and Wittig and co-workers (Ref. 37) are illustrated together with our proposed ionization scheme. The pump pulse in all the schemes is chosen close to 400 nm in order to excite the \(^2\)\(B_2\) state close to the dissociation limit on the \( \tilde{X} \)\(^2\)\(A_1\) state. As the result of internal conversion, the electronic character of the optically prepared state evolves in time. This can be detected by following the evolution of the photoelectron spectrum.

The difficulty in the case of NO\(_2\) is that the ground state of the cation and the Rydberg “stepping stone” states are all linear whereas the conical intersection between
the $\tilde{X}^2A_1/\tilde{A}^2B_2$ valence states occurs around $\alpha = 114^\circ$ so the ionization cross section is expected to vary considerably with bending angle.

![Graph](image)

**Fig. 3.** The total NO$^+$ ion signal recorded as a function of the delay of a probe pulse centered at 266 nm. The energies of the pump (400 nm) and probe (266 nm) pulses were 15 and 5 μJ, respectively. The decay of the NO$^+$ transient can be fit by forward convolution with a 90 fs laser pulse to a biexponential function with time constants of 90±10 and 4000±400 fs and weightings of 72% and 28%, respectively, as shown by the solid line in the figure. The inset shows the velocity map ion image recorded at the peak of the transient.

The insets show the velocity map ion images for the two species at zero time delay. The striking observation of kinetic energy release in the NO$^+$ signal at time zero immediately suggests that the ionization scheme is more complex than that just outlined, and is one of the main results of this study that needs to be explained. When examined in more detail, Fig. 5, the NO$^+$ signals also exhibit structure indicative of wave packet motion. The data shown in the figure come from three experimental runs taken at different temporal resolution recorded over 2 days. Each experimental run consisted of between 10 and 12
sequences. Figures 3 and 4 show the total ion signals, integrated over all recoil speeds, measured for NO\(^+\) and NO\(_2^+\), respectively, as a function of the pump (400 nm)-probe (266 nm) delay. Each sequence measured the total ion count for the average of four ion images taken at each time step. The points represent the average signal over the whole sequence, and the error bar one standard deviation. Although the oscillations in the total ion signal are small, the statistics are convincing.

![Graph showing ion counts vs. 266 nm delay](image)

Fig. 4. The total NO\(_2\) ion signal recorded as a function of the delay of a probe pulse centered at 266 nm. The energies of the pump (400 nm) and probe (266 nm) pulses were 15 and 5 μJ, respectively. The inset shows the velocity map ion image recorded at the peak of the transient.
IV.4. Discussion

Nitrogen dioxide is unusual in that more NO$^+$ ions are produced than NO$_2^+$ at low excitation energy, both by electron-impact ionization and by photoionization, which is explained by the fact that the neutral is bent while the ion is linear [34]. There was consequently uncertainty as to the ionization potential (IP) of the molecule in the early literature. The NIST Chemistry WebBook database [35] gives the evaluated adiabatic IP as 9.586±0.002 eV. This rather precise value was obtained by Haber et al. [36] in a three-
Dissociative multiphoton ionization of NO₂.

A color experiment in which two-photon excitation was used to excite the bent molecule to a linear Rydberg state from which a third photon could be used to ionize the molecule without the Franck-Condon constraints encountered in direct photoionization or electron-impact measurements with values ranging from 10.4 to 11.23 eV.

Davies et al. have studied the time-resolved photoelectron angular distributions during the photodissociation of NO₂ in a one-color pump-probe experiment at 375.3 nm [25]. Their data can be interpreted as being due to three-photon excitation to an unspecified electronic state of NO₂ which dissociates to NO(C 3Π) + O(3P). A fourth photon later ionizes NO(C 3Π) whereafter the photoelectrons and photoions can be imaged in coincidence. The two-color experiments of López-Martens et al. [30] using a 400 nm pump and 800 nm probe can be interpreted in terms of a similar mechanism but now with the pumped state of NO₂ dissociating to NO(A 2Σ⁺) + O(3P). The initially excited electronic state of NO₂ cannot be the same in the two mechanisms since three photons of 400 nm do not have enough energy to reach the C state of NO, 9.579 eV above the ground state of NO₂.

In our experiments, a prompt NO⁺ signal is observed as a function of the 266 nm delay (Fig. 3). The best fit rise time of the signal is ~57 fs (although since this is of the same order as the cross-correlation time of the two pulses all we can say is that the rise time is on the same time scale as the excitation). The kinetic energy of the NO⁺ fragment can be obtained by Abel inversion of the ion image shown in the inset to Fig. 3. The ion KER spectrum is shown in Fig. 6. It is quite broad and unstructured and peaks about 260 meV. If we assume three-photon excitation at 400 nm to a state that dissociates to NO(A 2Σ⁺, v = 0) + O(3P) according to the mechanism proposed by López-Martens et al. then the total excess energy from the dissociation would be 0.734 eV (the kinetic energy (KER) in the NO(v=0) moiety, for this channel is 0.255 eV). One could imagine similar photofragmentation pathways to the NO(B 3Π) state or, possibly, the a 4Π state, where the maximum KER in the zeroth vibrational state of the NO channel would be 0.17 eV or 0.421 eV, respectively. However, the last pathway agrees with the observed KER, but the a 4Π channel is spin forbidden.
The immediate absorption of a fourth 266nm photon from the intermediate state is capable of producing a NO$^+$ fragment with sufficient excess energy to agree with the observations. The excess energy for the processes

$$NO_2 \rightarrow ^3x^{400nm} NO_2^{**} \rightarrow ^{266nm} NO^+(\Sigma^+, v = 0) + O(^3P) + e^- + 1.6eV$$

is 1.6 eV, which would result in an ionic fragment with up to 0.54 eV of kinetic energy and the mechanism is a similar model of Davis et al.\[24\]. The difficulty with this interpretation is its oscillatory decay (Fig. 5). We could consider also the mechanism:

$$NO_2 \rightarrow ^3x^{400nm} NO(A^2\Sigma^+, v = 0) + O(^3P) + 0.734eV$$

where the total excess energy is 0.734 eV and the ionic fragment energy part is 34%, meaning 0.255 eV.
López-Martens et al. [27] observe a rise time of order 600 fs for the NO(A$^2\Sigma^+$) signal. This is similar to the 350–500 fs time scale for O-NO bond cleavage observed by Davies and company [24]. These times are more consistent with an indirect dissociation mechanism involving electronic predissociation similar to that observed for the $\tilde{A}$ $^2\Pi_1/\tilde{X}^2\Delta_1$ states. The prompt appearance of the NO$^+$ signal we observe is more consistent with a direct neutral dissociation involving a bending mode of the molecule, where the vibrational frequency varies from 560 cm$^{-1}$ in the H state to 750 cm$^{-1}$ in the $\tilde{X}$ state and is possibly as fast as 896 cm$^{-1}$ in the $\tilde{B}$ state [36]. Our observation of a rise time of order 600 fs for the NO(A$^2\Sigma^+$) signal agreed with those of López-Martens et al. [27].

Since three photons of 400 nm light are energetically equivalent to two of 266 nm, we could be observing the process:

\[
NO_2(\tilde{X}^2\Delta_1) \rightarrow ^{400nm} NO_2(\tilde{A}^2\Pi_2) \\
NO_2(\tilde{A}^2\Pi_2) \rightarrow ^{2x266nm} NO_2^{**} \rightarrow NO^+(1\Sigma^+, v = 0) + O(3P) + e^- + 0.045eV
\]

When we examine the decay of the total NO$^+$ signal (Fig. 3) we find that the data can be fit by the biexponential function $0.72 \exp(-t/90\pm10) + 0.28 \exp(-t/4000\pm400)$ with $t$ in fs (266 nm delay), which suggests that we are observing competing processes. The faster component is due to a three-photon excitation at 400 nm to a state that dissociatively ionizes on the absorption of a fourth 266 nm photon (process 4.1.). From the rapid rise time of the signal we conclude that the reaction coordinate for this channel is barrierless and via a multiphoton dissociation. The slower component, which is only observable for slow NO$^+$ ions, may be due to the alternative DMI scheme involving one-photon absorption of 400 nm light of the $\tilde{A}^2\Pi_2$ state followed by two-photon 266 nm excitation to another highly excited state of NO$_2$ which auto ionizes to NO$^+(1\Sigma^+) + O(3P)$ (process 4.3).

If this interpretation were correct, we would expect the NO$^+$ signal at long times to decay on a time scale consistent with the internal conversion rate of NO$_2\tilde{A}^2\Pi_2$ to $\tilde{X}^2\Delta_1$. This is indeed the case. For long 266 nm delays a decay time of 4000±400 fs is entirely
consistent with the previous observations of Ionov et al. [12, 37] and of Abel et al. [15]
bearing in mind that the 400 nm pump laser in our experiments is broad and excites zero-
order levels in the NO₂ \( \tilde{A}^2B_2 \) state both above and below the dissociation limit on the
\( \tilde{X}^2A_1 \) state PES.

Interestingly when examined at higher resolution the decay of the NO⁺ signal
exhibits oscillations (Fig. 5). The Fourier transform of the decay trace reveals a
dominant contribution to the oscillations with a period of about 600 fs corresponding to
an energy level spacing of 55 cm⁻¹. If our interpretation of the origin of the NO⁺
transient is correct, this is the first direct measurement of the energy level density of the
coupled levels in the mixed \( \tilde{X}^2A_1/\tilde{A}^2B_2 \) state of NO₂ close to the conical intersection.
The resonance structure close to the threshold has recently been calculated by Abel et al.
[17] and has been proposed as the explanation for the step structure observed in the
energy dependence of the unimolecular rate constants by Wittig and co-workers
[12,14,37]. Our observation is consistent with this emerging picture of the dissociation
dynamics. However, other explanations for the wave packet motion cannot be ruled out.
For example, despite our contention that the dissociation of the initially pumped
electronic state of NO₂ in process 4.3 is direct, we might be observing competition with
an electronic predissociation via a conical intersection similar to that known to occur
between the ground and first excited electronic states.

Finally, we turn to the interpretation of the NO₂⁺ data shown in Fig. 4. The inset
shows the ion image obtained at time zero. There is some evidence of a N₂O₄ or cluster
contribution to the signal since some ions are observed with kinetic energy, but this is a
small contribution to the total signal. We have, however, already observed that the
photoionization of NO₂ is unusual in that close to threshold more NO⁺ is observed than
NO₂⁺ because of the geometry change upon ionization and the linear nature of the
Rydberg states. As mentioned in Sec. II, NO₂ does not absorb light at 266 nm, therefore
the long lived signal at negative 266 nm delays, i.e., 266 nm pumping, pertains to N₂O₄
and corresponds to ionization by three 400 nm photons. This accounts for the weak
signal and the dissociation of N₂O₄: the IP of N₂O₄ is 10.8±0.2 eV, although the vertical
value is higher at around 11.5 eV, and one photon of 266 nm light plus two of 400 nm
Dissociative multiphoton ionization of NO₂... yields 10.8 eV. Thus the absorption of a further photon of 400 nm light will provide more than enough energy to dissociate N₂O₄⁺ to form energetic NO₂⁺.

The majority of the NO₂⁺ ions have zero kinetic energy as expected for a signal from the monomer. We cannot attribute the majority of the observed NO₂⁺ signal to a mechanism involving one photon 400 nm pumping of the ²B₂ state followed by two-photon ionization via the 1 ²Π₆(3d) and 1 ²Σ⁺₄(3p) Rydberg states, because the decay (54±40 fs) of the signal for long 266 nm delay (~ picoseconds) is far faster than the decay of the UV fluorescence measured by Abel et al. [15]. However the decay of the NO₂⁺ signal is comparable to the rise time of the NO⁺ signal we measure. This observation fits with our proposed NO⁺ production mechanism and suggests that most of the NO₂ population is lost through a dissociative ionization route, such as (4.1), rather than by internal conversion to the X²A₁ state followed by dissociation. There is, however, a noticeable plateau to the long time decay of the NO₂⁺ signal that persists for several picoseconds. This is most likely due to NO₂ ³B₂ molecules pumped to levels below the dissociation threshold. However, our signal-to-noise ratio is not yet good enough to detect recurrences in this signal which would be expected as population oscillates between the coupled electronic states. The growth in the NO₂⁺ signal is consistent with 400 nm pumping of the NO₂ ³B₂ state followed by two-photon ionization, but the interpretation is clouded by the potential interference from the presence of N₂O₄ in the sample.

IV.5. Conclusions

We have studied dissociative multiphoton ionization (DMI) of NO₂ by time-resolved velocity map imaging in a two-color pump-probe experiment using the 400 and 266 nm harmonics of Saclay femtosecond laser facility (SLIC). We observe that most of the ion signals appear as NO⁺ following DMI. As a function of 266 nm delay, the total NO⁺ ion signals exhibit biexponential decay.

0.72 exp(-t/90±10) + 0.26 exp(-t/4000±400)
with τ in fs, and ~600 fs period oscillations due to wave packet motion are also observed. Close to the cross correlation of the two pulses the NO+ ions are observed to have ~280 meV peak kinetic energy. This value is consistent with, but not exactly (0.255eV) in accord with, the three-photon dissociation mechanism

\[ \text{NO}_2 \rightarrow 3x400\text{nm} \ NO(A^2\Sigma^+) + O(3P) + T_{\text{KER}}(0.734\text{eV}) \]

which has previously been proposed by López-Martens et al. [27]. These earlier investigations had observed the process by pump-probe depletion spectroscopy of the NO \( A^2\Sigma^+ \) state with a subsequent 800 nm pulse. In our experiments the resulting NO \( A^2\Sigma^+ \) molecules could be ionized by a subsequent 266 nm pulse with pretty close ~255 meV of kinetic energy in the \( v = 0 \) channel. Our observation of a rapid rise time to the NO+ signal coupled with the 280 meV kinetic energy release suggests that this mechanism is operating in which a component of the photoions arises from a dissociative multiphoton ionization channel involving the absorption of a fourth 266 nm photon from the bending mode of the pumped state when the NO moiety is still essentially bound to the O atom.

Some NO+ signal is also observed with low kinetic energy release. These ions could be produced by the alternative mechanism with a total excess energy of 15 meV. Some support for the possibility of this channel comes from our observation of a small number of NO2+ ions at very long 266 nm delays which suggests that at least some NO2 (\( \tilde{A}^2\Sigma_B^2 \)) population is created in our experiments.

\[ \text{NO}_2(\tilde{X}^2\Sigma_A^1) \rightarrow 4x400\text{nm} \ NO_2(\tilde{A}^2\Sigma_B^2) \]

\[ \text{NO}_2(\tilde{A}^2\Sigma_B^2) \rightarrow 2x266\text{nm} \ NO_2^{**} \rightarrow NO^+(1\Sigma^+) + O(3P) + e^- \]

Oscillations indicative of wave packet motion are observed in the NO+ decay. These may measure the average energy level spacing between the resonant levels of the \( \tilde{A}^2\Sigma_B^2 / \tilde{X}^2\Sigma_A^1 \) states close to their conical intersection, but alternative explanations cannot be ruled out. For example, although our data suggest that the intermediate state pumped by three photons of 400 nm light dissociates directly it is possible that there is competition with an indirect route to NO(A^2\Sigma^+) + O(3P). Such a mechanism would be
consistent with the observations of López-Martens et al. [27], who observed an approximately 600 fs rise time in the NO(A $^2\Sigma^+$) signal.

Further work is ongoing in our laboratories to improve the energy resolution of the photoelectron imaging spectrometer used in these experiments. This will allow us a better analysis of the intermediate states involved in the DMI process.

References

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30. The angular resolution of the photoelectron images is unaffected in this configuration.


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Chapter V

Photolysis of NO$_2$ at multiple wavelengths in the spectral region 200-205 nm: a velocity map imaging study

Abstract

A study of the photodissociation dynamics of NO$_2$ in the 200-205 nm region using resonance enhanced multiphoton ionization (REMPI) in conjunction with the velocity map imaging technique (VMI) is presented. We chose this region because it allowed the use of a single laser to photodissociate the NO$_2$ molecule and probe both the O($^1$D$_2$) fragment using (2+1) REMPI via the 3p'$^3$P$_1$ state at 2 × 205.47 nm and the 3p'$^1$F$_3$ state at 2 × 203.5 nm, and the O($^3$P$_j$) fragments using (2+1) REMPI via the 4p $^3$P$_j$ states around 2 × ~200 nm. Translational energy and angular distributions are extracted from the O($^1$D) and O($^3$P) product images. A growth in the population of highly excited vibrational levels of the NO X($^2$Π) co-fragment is found as the dissociation wavelength decreases. These are compared with similar trends observed previously for other triatomic O-atom containing molecules. Detailed information on the electronic angular momentum alignment of the $^1$D$_2$ state is obtained from analysis of the polarization sensitivity of the O($^1$D) images using the two resonant intermediate states. The angular dependence of the potential energy in the exit channels is examined using long-range quadrupole-dipole and quadrupole-quadrupole interaction terms, from which molecular-frame multipole moments of the total angular momentum of the recoiling O atoms have
been calculated. Comparison with the experimentally derived multipole moments is used to help provide insight into the dissociation mechanism.

V.1. Introduction

The NO\(_2\) molecule is photolytically active in the UV spectral region (Fig. 1) where it is known to dissociate through two spin conserved channels according to reactions (1.1) and (1.2):

\[
\text{NO}_2 \overset{X(\tilde{2}A_1)}{\rightarrow} \text{NO}(\tilde{2}^3\Sigma^+) + \text{O}(\tilde{3}P) \lambda < 397.86 \text{ nm} \quad (1.1)
\]

\[
\text{NO}_2 \overset{X(\tilde{2}A_1)}{\rightarrow} \text{NO}(\tilde{2}^3\Sigma^+) + \text{O}(\tilde{1}D_2) \lambda < 243.85 \text{ nm} \quad (1.2)
\]

The NO-O bond energy \(D_0(\text{NO-O}) = 25128.5 \pm 0.2 \text{ cm}^{-1}\) was accurately obtained by Jost et al. [1] using a laser-induced fluorescence method and near-threshold photolysis. The O(\(^1\text{D}_2\)) electronic level of channel (1.2) lies 15867.9 cm\(^{-1}\) above the O(\(^3\text{P}_2\)) ground state of atomic oxygen produced in channel (1.1), and spin-orbit splitting of the NO(X \(\tilde{2}\Sigma^+\)) state is 119.82 cm\(^{-1}\).

Numerous previous experimental studies of NO\(_2\) photodissociation have measured the energy disposal and O(\(^3\text{P}_J\)) \(J=2,1,0\) branching ratios of the fragments produced via channel (1.1). For example, Busch and Wilson [2,3] worked with an effusive NO\(_2\) beam which was photolysed using a doubled ruby laser at 347.1 nm and detected the resulting fragments using time-of-flight mass spectrometry. They found equal populations of NO(v = 0, 1) and significant rotational excitation. Zacharias et al. [4], working at 337.1 nm found an inverted vibrational population distribution peaking at \(v_{\text{max}} = 2\), the maximum level energetically possible NO(v) level. Slanger and co-workers [5] investigated the internal energy distribution of NO following NO\(_2\) photodissociation in the 248-290 nm region and found a great propensity for the excess available energy to go into NO vibrational excitation. At 248 nm \(v_{\text{max}}=8\) and the distribution was found to peak sharply at \(v=7\). Miyawaki et al. [6] reported the spin-orbit state distribution of the O(\(^3\text{P}_J\)) fragments produced during NO\(_2\) photodissociation at 212, 266, 337 and 355 nm.
Their experiments employed a supersonic jet of NO₂ and LIF detection of O(³P₁) fragments. They found an O(³P₁) distribution of J=2:1:0 = 1.00:0.19:0.03 at 266, 337 and 355 nm, while the photolysis at 212 nm yielded 1.00:0.35:0.08 (a statistical distribution would be 1.00:0.60:0.20).

Other previous experimental studies of NO₂ photodissociation have measured the angular distributions of the fragments produced via channel (1.1). For instance, Busch and Wilson [3] showed by angular distribution measurements that photo-absorption occurs to the ¹B₂ electronic state, a state which is strongly coupled to the ²A₁ ground electronic state and which exhibits fast pre-dissociation to NO (X ²Π₁/₂, 3/₂) and O(³P₁) [7]. When using linearly polarized light, the photofragment angular distribution for NO₂ follows the well known equation, I(θ) = (1/4π)[1 + ßP₂(cosθ)], where θ is the angle between the photolysis laser polarization and the fragment velocity vector, and ß is the anisotropy parameter. If the molecule dissociates quickly relative to its rotational lifetime, then ß is given by the simple equation ß = 2P₂(cosχ) where χ is the angle in the molecular frame between the transition dipole moment and the velocity vector of the fragment. For prompt dissociation, measurement of the spatial anisotropy parameter, ß, therefore enables a determination of the geometry of the molecule at the time of dissociation, as long as the direction of the transition dipole moment is known. Since the ground state is totally symmetric (²A₁), the transition dipole will have the same symmetry as the excited state. This means for a transition to a ³B₂ upper state the transition dipole moment will be perpendicular to the C₂v axis and in the plane of the molecule. Should NO₂ dissociate from the same geometry as the ground state where the O–N–O angle is 134°, then the photofragment angular distribution would be described by ß=1.4. Hradil et al. [8] investigated the photolysis of NO₂ via the ¹B₂ upper state at 355 nm using the photofragment imaging technique. They found the same anisotropy parameter for both the O(³P₂) and NO fragments of ß=1.2±0.3 for both fragments. This value for ß was significantly larger than that originally determined by Busch and Wilson. The difference could be attributed to the fact that in a thermal beam the rotational period is comparable to electronic predissociation time. The average rotational period at 370 K (the temperature of Busch and Wilson’s experiments) is 224 fs.
compared to 5.5 ps at 15 K (the temperature of Hradil et al. experiments). Time resolved PHOFEX studies by Wittig and co-workers [9] have shown that the lifetime of the $1^3B_2$ for dissociation via channel (1.1) falls rapidly from 50 ps at 2-3 cm$^{-1}$ above threshold to below 7.7 ps by 25 cm$^{-1}$ of excess energy and to less than 0.8 ps at about 800 cm$^{-1}$ of excess energy. A study of both fragments from jet cooled NO$_2$ at 371.1, 354.7 and 338.9 nm was published by Demyanenko et al.[10]. They obtained the anisotropy parameter for O($^3P_2$) from measurements of the NO fragment. From their results it was deduced that, especially with photon energies closer to threshold dissociation, $\beta$ depends strongly on both the rotational and translational energy of the fragment.

In this study we excite the NO$_2$ molecule around to 200 nm to the presumed $2^3B_2$ state. In contrast to $1^3B_2$ state the $2^3B_2$ state is predissociative from its origin [11]. The absorption spectrum (Fig. 1) shows a progression of broad peaks above a continuum that reaches a local maximum around 220 nm. The lifetime of low lying rotational levels in the $^3Q_{R_0}$ branch of the (0,0,0) band at an excitation energy of 40 126 cm$^{-1}$ has been measured by Tsuji et al. [12] to be 41 ps. Here the dissociation is believed to proceed via internal conversion to the high lying vibrational states in the $1^3B_2$ state leading to vibrationally excited NO($X^2\Pi$) + O($^3P$). The (0,1,0) and (0,0,2) vibrational levels 525 and 718 cm$^{-1}$ above the (0,0,0) level respectively similarly lead to ground state products but the dissociation rate is much faster than the origin band (the lifetimes are 4.8 and 160 fs respectively [12,13]. The next vibrational level (1,0,0) of the $2^3B_2$ state lies ~300 cm$^{-1}$ above the second dissociation limit at 243 nm (40 125.85 cm$^{-1}$) at which channel (2) opens but the excited state lifetime, between 75 and 62 fs, is not markedly shorter than that of the (0,0,2) level. Some variation in the lifetimes of the subsequent three vibrational bands was noted by Tsuji and co-workers but no systematic dependance on the vibrational mode could be discerned and remained ~100 fs as the excess energy was increased.

Besides the study of Miyawaki et al. [6] at 212 nm, there have been only a few reports of NO$_2$ photodissociation product state distributions at energies above the second dissociation limit. Slanger and coworkers [14] reported photodissociation at 157 nm with NO detection by LIF. They found predominantly ground-state channel (1.1)
products with very high rotational (N≤73) and vibrational (ν≤21) excitation, even though channel (1.2) and higher channels (O(^1S) production, for example) are open at this VUV wavelength. Other studies, including the present report, have used optical excitation in the second band covering the 240-190 nm region shown in Fig. 1. In this region the O(^1D) quantum yield was found by Uselman and Lee [15] to increase from 0 at 243 nm to around 0.4 - 0.5 in the 230-210 nm region. This finding is in agreement with the linewidth study of Tsuji et al. [12] which concluded that the predissociation rate into channel (1.1) was high enough to compete with that into channel (1.2) since the linewidths just above and below the second ionization limit were approximately the same. However, at a slightly shorter wavelength Richter et al. [16] determined the yield ratio O(^1D):O(^3P) to be 7:1 by monitoring the temporal profile of O(^3P) production after photolysis at 212.8 nm laser light of effusive NO₂ using an N₂ or He buffer.

Shafer et al. [17] have reported (2+1) REMPI detection of O(^1D) following 205.47 nm photolysis of an effusive beam of NO₂ using a single laser for both dissociation and detection. They found an anisotropy parameter β=1.32, indicative of prompt dissociation. Ahmed et al. [18] have reported a one color experiment at ~226 nm to dissociate NO₂ and simultaneously detect the O(^3P_j) and NO fragments by (2+1) and (1+1) REMPI, respectively. NO detection provides information on both the NO + O(^3P) and NO + O(^1D) channels for the selected NO quantum state. They found the anisotropy parameter β=1.32 for the O(^3P₀) atom and a different value of β ~ 0.6 for the O(^1D) channel. A branching ratio of O(^1D):O(^3P)= 1.00:0.01 was extracted from the NO(v=0, N=16) fragment image in a (1+1) REMPI process. In further work, this group has also studied the dissociation at 212.8 nm with subsequent detection of O(^3P_j) fragments at 226 nm using the velocity map imaging technique [19]. Their two-laser experiment allowed the study of angular momentum alignment in the O(^3P_j) product (O(^3P₀) has zero total angular momentum and thus no alignment) by changing the probe laser polarization. The results of reference [19] showed that the dominant mechanism responsible for the alignment is an incoherent parallel excitation of the parent molecule.
In our experiment velocity map imaging is applied to study the energy partitioning and angular distribution of the O($^3P_j$) and O($^1D$) photofragments produced by photodissociation of the NO$_2$ molecule at wavelengths between 200.64 - 205.47 nm. O($^3P_j$) detection takes place by (2+1) REMPI via the 1s$^2$2s$^2$2p$^4$4p($^3P_j$) Rydberg state in the ~200 nm region instead of the usual (2+1) REMPI via the 1s$^2$2s$^2$2p$^4$3p($^3P_j$) state in the ~226 nm region. One advantage of this detection scheme is that the wavelengths used in the standard detection method for O($^1D_2$) atoms [16] also fall in the same region. In a separate paper [21] we show that the polarization and J-dependent sensitivity using the 4p($^3P_j$) state is similar to detection via the 3p($^3P_j$) state, and the overall sensitivity is a factor of ~7 lower. The O($^1D_2$) transitions are at 205.47 and 203.82 nm, via the 3p$^1P_1$-$^1D_2$ and 3p$^1F_3$-$^1D_2$ states, respectively. We describe here one-laser experiments where dissociation takes place at the wavelength tuned for the REMPI detection process.
Using the $4p(3P_j)$ resonance we can thus compare $O(3P_j)$ and $O(1D)$ data at similar dissociation energy. In reference [21] we compare yield and polarization sensitivity factors for the two $O(3P_j)$ detections schemes and the two $O(1D)$ schemes. Our present one-laser experiments offer very limited polarization information for $O(3P_{21})$ detection. For $O(1D_2)$ detection the $^1P_1$ and $^1F_3$ states have quite different two-photon angular-dependent alignment sensitivity for each $|m_J|$ state ($m_J = -2,-1,0,1,2$). Polarization information can thus be extracted by comparing the two detection pathways following the assumptions and methods introduced by Mo and Suzuki [22].

Photodissociation studies of other O-atom containing triatomic molecules such as $O_3$ [23], $N_2O$ (Neyer et al. [24], Teule et al.[25]), $SO_2$ [26], $OCS$ [27] and $OClO$ [28] have been reported, which can be compared with the present data. In particular, we find that an $m_J$-dependent anisotropy parameter is necessary in the alignment analysis of our $O(1D)$ images. We use a long-range quadrupole-dipole and quadrupole-quadrupole interaction analysis similar to that used for related studies of $N_2O$ and $SO_2$. From this analysis the molecular-frame multipole moments of the total angular momentum of the recoiling O atoms have been calculated. In contrast to $NO_2$ and $SO_2$, no potential energy surfaces are available for states correlating to the second dissociation limit of $NO_2$. The standard approach of comparing the adiabatic and diabatic limits for connecting the optically excited state to the dissociation products is thus not possible at this moment in the case of $NO_2$. Instead, we compare the measured product distribution with those predicted for different adiabatic states combining the $O(1D)$ and $NO(2^3Π)$ sub-units in $C_s$ symmetry.

In section 2 we described the experimental set-up used. In section 3 we present the measured images, their data analysis and results. In section 4 we discuss the long-range model. In section 5 we summarize our results for this one-laser study.

V.2. Experimental set-up

The experiment was performed on a new on-axis velocity map imaging set-up based on the design of Eppink and Parker [30]. Briefly, it consists of two vacuum chambers
evacuated to $2 \times 10^{-7}$ Torr: the source chamber and the detection chamber, which are separated by a gate valve. During the experiment the gate valve is open and the chambers are connected by a 2 mm skimmer on axis with respect to the electrostatic lens. Optical access to the detection chamber is provided between the repeller and extractor lenses by 4 VUV windows. This allows two laser beams to propagate perpendicular to each other and to the TOF axis. The electrostatic lens accelerates the charged particles produced by laser ionization through a 34 cm field-free TOF tube to the position sensitive detector.

The photolysis light is generated by a dye laser operating at ~600 nm, pumped by the 2nd harmonic of a Nd:YAG laser. By frequency tripling using a KDP crystal for doubling followed by mixing in a BBO crystal, wavelengths were selected at 200.64 nm, 200.96 nm, 201.1 nm, 203.8 nm and 205.47 nm. Each of these chosen wavelengths is used to photodissociate and subsequently probe the oxygen product in a one-laser experiment.

A pulsed supersonic beam of 0.5% NO$_2$ in He is directed along the TOF axis. In order to avoid NO$_2$ clustering a 0.4 bar backing pressure of the molecular beam was applied. The charged photofragments were then projected onto a gated dual microchannel plate (MCP) assembly, followed by a phosphor screen. The CCD camera (PixelFly, size: 640x480 pixels) records the 2D distribution on the phosphor screen. Mass selectivity is obtained by gating the front MCP. Typically, 5000-10000 laser shots were averaged to collect the raw 2D image. The full 3D fragment distribution was then reconstructed from the raw 2D image by utilizing an inversion algorithm [30]. The inverted image represents a slice through the middle of the reconstructed 3D fragment distribution from which fragment translational distribution is extracted.

The 200-205 nm laser light (~ 1mJ/pulse, 0.5cm$^{-1}$ bandwidth) was focused onto the molecular beam by a 20 cm lens. Due to the Doppler width of the oxygen fragments, the probe laser frequency was scanned over the entire Doppler profile to ensure that all product velocities were detected with equal sensitivity.
V.3. Results and discussion

V.3.1. O(3P_J) detection from photodissociation of NO2 at 200.64, 200.96, and 201.98nm

UV photodissociation of NO2 induced by a pulsed laser tuned to the REMPI transition for O(3P_2) detection at 200.64 nm initiates the photodissociation process:

\[ \text{NO}_2 + h\nu_{200.64 \text{ nm}} \rightarrow \text{NO}(\text{X}^2\Pi_{\frac{1}{2}}) + \text{O}(3P_2) + 3.116 \text{ eV.} \]  \hspace{1cm} (1.3)

Figure 2a) displays raw O⁺ images, which are 2-D projections of the O⁺ 3-D Newton spheres, taken at three different wavelengths: 200.64 nm, 200.96 nm and 201.098 nm, used for O(3P_J) REMPI for J = 2, 1 and 0, respectively. Abel-transformed images are shown in Fig. 2b). All O(3P_J) images were taken in the same condition of backing pressure, ~0.4 bar, and laser intensity, 0.9 mJ/pulse. The laser electric field polarization direction E is horizontal in the laboratory frame (i.e. parallel with the surface of the detector) which is necessary for the reconstruction of the 3D velocity distribution from the original 2D ion data. Ion intensities in these representations increase from black to white. The relative J=2:1:0 yield found by integrating the entire images under the same conditions was 1 : 0.0203 : 0.0188, in large disagreement with a statistical 1 : 0.6 : 0.2 ratio. It appears that the wavelength used for REMPI of O(3P_2) at ~200 nm is accidentally resonant with an absorption peak of our jet-cooled NO2 sample.

Because the general appearance of the three O(3P_J) images is similar, we suggest that this is a simple intensity effect and does not significantly change the angular or kinetic energy information. In each of the images several well resolved sharp rings peaking at radii close to the center of the detector are discernible. The high intensities observed at small pixel radii indicate that the major fraction of the O(3P_2) atom is released with very low velocities in the dissociation process. In fig. 2(c) the vibrational level of the NO co-fragment is indicated in the O(3P_2) translational distribution. The inner ring of the image corresponds to \( v_{\text{max}} = 14 \), the highest possible NO(\text{X}\Pi) vibrational level. Rings for \( v=13 \) and \( v=12 \) are also present and the largest diameter ring corresponds to NO(\text{X}\Pi) \( v \sim 7 \).
Note that the 123.14 cm$^{-1}$ NO($^2\tilde{\Pi}_{3/2} \leftarrow ^2\Pi_{1/2}$) spacing should result in a splitting of the rings which is not resolved in this study, most likely due to overlapping rotational levels.

The vibrational spacing observable in the kinetic energy distributions are in good agreement with the known vibrational constants of NO($^\chi^2\tilde{\Pi}_{1/2,3/2}$) from the NIST database. Many of the vibrational levels are well-resolved, especially to those corresponding to the low fragment kinetic energy distribution [25]. Also apparent is the lower rotational energy spread for the high vibrational levels v=12-14 compared to the lower levels v=7-11. The O($^3\tilde{P}_0$) image reported by Ahmed et al. for photodissociation of NO$_2$ at 226 nm is quite broad and without structure, similar to the outer rings v=7-11 of our image at 200 nm [18]. At our higher excitation energy we see the growth of a new
set of low kinetic and rotational energy, maximally vibrationally excited NO molecules, reminiscent of our OClO study [28] where, again at the blue edge of the absorption spectrum, extremely highly vibrationally exited OCl(ν=22) was the only product observed. Similar effects are seen for ultraviolet photodissociation of ozone [23], where highly vibrationally excited \( \text{O}_2 \text{X}^2\Sigma_g^+(\nu>26) \) is observed for photodissociation at the blue edge of the absorption spectrum.

Angular information from these \( \text{O}(^3\Pi_j) \) images is complicated by the alignment sensitivity of the linearly polarized detection laser. If we separate the high (ν=14-12) and low (ν=11-7) vibrational components then the anisotropy parameter, \( \beta \), determined from fitting the experimental data using \( I(\theta) = \frac{1}{4\pi} [1 + \beta \cos^2 \theta] \), was found to be \( \beta(J=2:1:0) = 0.94:0.83:0.55 \) for ν=14-12, and \( \beta(J=2:1:0) = 1.04:1.16:1.00 \) for ν=11-7. Because our experiment only employs a single laser we are not at liberty to independently change the polarisation of the photolysis and probe photons. Consequently \( \beta \) is only meaningful in our experiment for the \( J=0 \) component, where we find for the comparable ν=11-7 band a slightly lower value \( \beta = 1.00 \) at 200 nm than the value of \( \beta = 1.30 \) found by Ahmed et al. at 226 nm [18]. A two-color experiment with different polarization geometries such as that of reference [18] would yield a more complete picture of the dissociation dynamics for the \( \text{O}(^3\Pi_j) \) channel at ~200nm.

V.3.2. \( \text{O}(^1\text{D}) \) detection produced via photodissociation of \( \text{NO}_2 \) at 205.47 and 203.81 nm

UV photodissociation of \( \text{NO}_2 \) induced by a pulsed laser tuned to the REMPI transition for \( \text{O}(^1\text{D}) \) detection at 205.47 nm initiates the photodissociation process:

\[
\text{NO}_2 + h\nu_{205.47\text{nm}} \rightarrow \text{NO}(\text{X}^2\Pi_{1/2,3/2}) + \text{O}(^1\text{D}) + 0.95 \text{ eV.} \quad (1.4)
\]

Figure 3(a) displays raw \( \text{O}^+ \) images taken at 205.47 nm and 203.81 nm, used for \( \text{O}(^1\text{D}) \) REMPI via the \( 3\pi^0 \text{P}_1\text{D}_2 \) and \( 3\pi^0 \text{F}_3\text{D}_2 \) states, respectively. Abel-transformed images are shown in Fig. 3b). The translational distribution for \( \text{O}(^1\text{D}) \) Figure 3(c) shows peaks
corresponding to vibrational levels 0-4 of the NO co-fragment. The most populated vibrational level of NO ($^3\Pi_{3/2}, ^3\Pi_{1/2}$) is $v=4$ followed by $v=3$ (see Fig. 3(b), (c)).

![Image](image_url)

Fig. 3 (a) Raw image and (b) 2-D slices from reconstructed 3-D recoil distribution of O($^1D_2$) atoms resulting from photolysis of jet-cooled NO$_2$ recorded by 2+1 REMPI via the $^1P_1$ and $^1F_3$ Rydberg states at an excitation wavelength of 205.47 and 203.81 nm respectively. (c) The corresponding translational energy distributions.

Table I. Gaussian fit parameters for the O($^1D$) (via $^1P$) translational energy distribution shown in Fig. 4 (below).

<table>
<thead>
<tr>
<th>NO($v$)</th>
<th>Peak area (a.u.)</th>
<th>Energy (eV)</th>
<th>Calc. energy (eV)</th>
<th>Width (eV)</th>
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<tbody>
<tr>
<td>4</td>
<td>3.8</td>
<td>0.026</td>
<td>0.026</td>
<td>0.06</td>
</tr>
<tr>
<td>3</td>
<td>2.6</td>
<td>0.213</td>
<td>0.249</td>
<td>0.09</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td>0.35</td>
<td>0.474</td>
<td>0.095</td>
</tr>
<tr>
<td>1</td>
<td>0.6</td>
<td>0.52</td>
<td>0.703</td>
<td>0.1</td>
</tr>
<tr>
<td>0</td>
<td>0.8</td>
<td>0.68</td>
<td>0.936</td>
<td>0.17</td>
</tr>
</tbody>
</table>

*a* Vibrational levels for NO co-fragment reflected in the O($^1D$) image.

*b* The area of the Gaussian-fit for each vibrational level.

*c* Fitted peak center position.

*d* Calculated energy levels using NO(J=0) constants from NIST.

*e* Half-widths of the fitted peaks.
Similar to all previous studies of channel (2) NO\textsubscript{2} photodissociation, a highly inverted vibrational distribution is observed where the maximum possible vibrational level is the most populated. The width of the peaks shown in figure 3 provides information about the rotational energy of the NO co-fragment. Gaussian fits to the O(\textsuperscript{1}D\textsubscript{2}) translational energy distribution recorded via the \textsuperscript{1}P\textsubscript{1} Rydberg state are shown in Fig. 4 and Table I. The results given in figure 3 (b),(c) reveal a noticeable change in the ion intensities. In both situations the fig.3(c) shows up intensities and widths for the lowest fragment which is more or less the same. At the 203.8 nm experiment, for the more energetic fragments the intensities and the widths of these peaks are higher. Also, at 203.8 nm we found $\beta$=0.3 (see Table 2).

Table II. (O\textsuperscript{1}D\textsubscript{2}) measured values of anisotropy parameter $\beta$ for several vibrational states of NO

<table>
<thead>
<tr>
<th>product/nm</th>
<th>$\beta$ (NO\textsubscript{2}v=0)</th>
<th>$\beta$ (NO\textsubscript{2}v=1)</th>
<th>$\beta$ (NO\textsubscript{2}v=2)</th>
<th>$\beta$ (NO\textsubscript{2}v=3)</th>
<th>$\beta$ (NO\textsubscript{2}v=4)</th>
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</thead>
<tbody>
<tr>
<td>O\textsuperscript{1}D\textsubscript{2}/205 nm</td>
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<td>1.1</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>O\textsuperscript{1}D\textsubscript{2}/203 nm</td>
<td>0.3</td>
<td>0.3</td>
<td>0.6</td>
<td>0.6</td>
<td>0.3</td>
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</tbody>
</table>

Both O(\textsuperscript{1}D\textsubscript{2}) images show a broad translational energy distribution radius of the image, caused by the variable amount of rotational energy taken up by the NO fragment. Compared to the \textsuperscript{1}F\textsubscript{3}<\textsuperscript{1}D\textsubscript{2} image (recorded at 203.81 nm), the angular distribution of the \textsuperscript{1}P\textsubscript{1}<\textsuperscript{1}D\textsubscript{2} image (recorded at 205.47 nm) is more peaked along the vertical axis, and shows a dimple on the horizontal axis. The differences in the angular distribution in the O (\textsuperscript{1}D\textsubscript{2}) images using different detection schemes arises from the variation in the detection probabilities for the various $m$-levels in the two ionization routes. For analysis, the Abel-inverted images are divided into shells with different radii corresponding to a range of translational energies, where each shell corresponds roughly...
to the fitted Gaussians. The results are summarized in Table II. Each shell corresponds to a range of rotational levels in the NO fragment.

Fig. 4. Gaussian representation fit to the NO vibrational distribution determined from the O(\(^1\)D) kinetic energy distribution measured at 205.47nm shown in Fig. 3c).

V.4. Ab initio calculation and semi-classical model

V.4.1. Polarization effects in the velocity map image

Our interpretation of the O(\(^1\)D) imaging results is based on the model of Mo and Suzuki [22,31] which we summarize here. The observed ion angular distribution is
written as the product of the photofragment angular recoil distribution \( I_{\text{rec}}(\theta) \) and the detection efficiency \( I_{\text{det}}(\theta) \)

\[
I_{\text{ion}}(\theta) = I_{\text{rec}}(\theta) I_{\text{det}}(\theta),
\]

where \( \theta \) is the angle between the photolysis laser polarization \( \vec{E} \) and the fragment velocity \( \vec{v} \). The fragment distribution for a one photon transition \([32]\) is given by

\[
I_{\text{rec}}(\theta) = \frac{1}{4\pi} [1 + \beta_v P_2(\cos \theta)],
\]

where \( P_2(\theta) = \frac{3}{2} - 2 \) is the second order Legendre polynomial and \(-1 \leq \beta_v \leq 2\) is the anisotropy parameter, which depends on the vibrational quantum number \( v \) of the cofragment. The detection efficiency depends on the polarization of the photofragment with respect to the polarization of the probe laser \([31]\):

\[
I_{\text{det}}(\theta) = \sum_k \rho^{(k)}_{0,\text{PF}} P_k(J_f, J_i).
\]

where the \( P_k(J_f, J_i) \) are \( J \) dependent line strength (geometric) factors and the \( \rho^{(k)}_{0,\text{PF}} \)

are the zero components of density matrix multipole moments of rank \( k \) \([33]\) in the reference frame defined by the probe laser polarization (PF - probe frame). For a two photon transition, the index \( k \) runs through even numbers from 0 to 4. For linearly polarized light \((s=0)\), where the initial and final atomic angular momenta are different, i.e., \( J_i \neq J_f \) and for circularly polarized light \((s=\pm1)\) Mo and Suzuki \([31]\) give analytic expressions involving \( 3j \) and \( 6j \) symbols for the line strength factors. As they point out, in many practical applications, including ours, only the relative ratio of the geometrical factors with respect to that for \( k = 0 \) is actually needed:

\[
\tilde{P}_k(J_f, J_i) = \frac{P_k(J_f, J_i)}{P_0(J_f, J_i)} = \frac{5\sqrt{2k+1}\sqrt{2J_i+1}(-1)^{J_f+J_i} \times \left( \begin{array}{c} 2 & 2k \\ 2s-2s0 \end{array} \right) \left( \begin{array}{c} J_i \ J_f \\ 2 \ 2J_f \end{array} \right)}{\sqrt{2k+1}\sqrt{2J_i+1}(-1)^{J_i+J_f} \times \left( \begin{array}{c} 2 & 2k \\ 2s-2s0 \end{array} \right) \left( \begin{array}{c} J_f \ J_i \\ 2 \ 2J_i \end{array} \right)}.
\]

In the present experiment the O \( ^1D_2 \) atoms are detected at 205.47 nm through the \( 3p^1P_1 \leftrightarrow ^1D_2 \) two photon resonance, for which we have

\[
\tilde{P}_2(1,2) = -\frac{5}{\sqrt{14}} = -0.598 \quad \text{and} \quad \tilde{P}_4(1,2) = -\frac{8}{\sqrt{7}} = -1.069.
\]

We also used the
Chapter 5

The zero component of the rank \( k \) multipole moments in the probe frame, \( \rho_{0,\text{RF}}^{(k)} \), are related to the multipole moments in the recoil velocity frame (RF) \( \rho_{r,\text{RF}}^{(k)} \) through

\[
\rho_{0,\text{RF}}^{(k)} = \sum_{q=-k}^{k} \rho_{r,\text{RF}}^{(k)} C_{kq}(\theta, \phi),
\]

where the \( C_{kq} \) are modified spherical harmonics and \( \theta, \phi \) are the polar angles of the recoil velocity \( \vec{v} \) in the probe frame, which in the present one-laser experiment has \( \vec{e} \) along the Z-axis. To limit the number of degrees of freedom in our theoretical model of the dissociation to be described below we will make the following additional assumptions about the atomic angular distribution [22]: (1) the distribution is cylindrically symmetric around the recoil velocity \( \vec{v} \) and (2) the distribution is independent of \( \vec{v} \). With these assumptions only the \( q=0 \) component of \( \rho_{r,\text{RF}}^{(k)} \) is nonzero and it can be expressed in terms the recoil frame \( m \) state fractional population \( f_m \) as

\[
\rho_{0,\text{RF}}^{(k)} = \sum_{m=-J_f}^{J_f} (-1)^{J_f-m} \sqrt{2k+1} \binom{J_f}{J_i} \binom{J_i}{m} f_m
\]

Note that, because of the symmetry of the 3-j symbol, \( \rho_{0,\text{RF}}^{(k)} \) can be re-expressed in terms of \( p_0^{(1)} = f_0 \) and \( p_{m}^{(0)} = f_{m} + f_{-m} \) with \( m>0 \). Combining Eq. (1.5) to (1.7) with Eq. (1.9) and using \( C_{k,0}(\theta, \phi) = \hat{P}_k(\cos \theta) \) we can express \( I_{\text{ion}} \) as

\[
I_{\text{ion}}(\theta) \sim \beta_v \sum_{k} \rho_{0,\text{RF}}^{(k)} \hat{P}_k(J_f, J_i) \hat{P}_k(\cos \theta) = \sum_{k} c_k \hat{P}_k(\cos \theta)
\]

Expanding the product of Legendre polynomials using

\[
P_z(z)P_p(z) = \sum_{l=\max(0,k-2)}^{k+2} |\langle 20k0|l0 \rangle|^2 P_l(z)
\]

we find

\[
c_k = \rho_0^{(j)} \hat{P}_l(J_f, J_i) + \beta_v \sum_{k} |\langle 20k0|l0 \rangle|^2 \rho_{0,\text{RF}}^{(k)} \hat{P}_k(J_f, J_i),
\]
for which the non-zero terms are

\[
\begin{bmatrix}
  c_0 \\
  c_2 \\
  c_4 \\
  c_6 \\
\end{bmatrix}
= \begin{bmatrix}
  1 & \frac{1}{5} \beta, & 0 \\
  \beta, & 1 + \frac{2}{7} \beta, & \frac{2}{7} \beta, \\
  0 & \frac{18}{35} \beta, & 1 + \frac{20}{77} \beta, \\
  0 & 0 & \frac{5}{11} \beta, \\
\end{bmatrix}
\begin{bmatrix}
  \rho_{0,RF}^{(0)} \\
  \rho_{1,RF}^{(1)} \\
  \rho_{0,RF}^{(2)} \\
  \rho_{1,RF}^{(3)} \\
\end{bmatrix}
\]

Since the absolute intensities are not determined, the experimental data consists of the moments \( c_j = c_j/c_0 \), for \( j = 2, 4, 6 \) for the two detection schemes, i.e., there are six independent parameters for each dissociation channel.

V.4.2. Electrostatic model for fragment polarization

To interpret the fragment polarization we apply a model similar to one developed previously to describe the photodissociation reactions \( \text{N}_2\text{O} + h\nu \rightarrow \text{N}_2 + \text{O}(^1D_2) \) [25] and \( \text{SO}_2 + h\nu \rightarrow \text{SO}(^3\Sigma^+) + \text{O}(^3P_J) \) [26]. In this model we compute the adiabatic electronic wave functions for the \( \text{O}(^1D_2) \) atom as a function of the Jacobi angle \( \gamma \) (with \( \gamma = 0 \) corresponding to linear \( \text{ON} \rightarrow \text{O} \)) for some value of the distance \( R_c \) between the \( \text{O} \) atom and the center of mass of the \( \text{NO} \) moiety. For the atom we include the five degenerate \( ^1D_2 \) states \( |\lambda = 2, \mu \rangle, \mu = \lambda, \ldots, \lambda \) and we only consider first order electrostatic interactions. Since the \( \text{NO} \) molecule is produced in a \( ^2\Pi \) state each atomic state gives rise to two potential energy surfaces of \( A' \) and \( A'' \) symmetry which are coupled by spin-orbit interaction. In the experiment, however, the two spin-orbit states of the \( \text{NO} \) fragment are not resolved and hence we compute the multipole moments of \( \text{NO} \) that are used in the model by taking the average over the two \( \Pi \) components, effectively treating \( \text{NO} \) as a \( \Sigma \) state, which we denote as \( |\chi\rangle \). The 5x5 interaction matrix in a molecular frame defined
with the departing O atom on the positive z-axis and the NO molecule in the x-z plane is given by [26,34].

\[ V = \sum (-1)^{l_a+l_b} \frac{\langle \hat{Q}_{a} | \hat{A} | \hat{Q}_{b} \rangle | \alpha \rangle}{R_{c}^{l_a+l_b}} \begin{pmatrix} (2l_a+2l_b+1)! \langle l_a, l_a+l_b | l_a, l_a+l_b \rangle \int_{-\mu} m_{\mu} \mu_{\mu} \right) C_{m_{\mu}}^{m_{\mu}} \psi(0) \end{pmatrix} \tag{1.15} \]

The eigenvalues of this matrix yield the adiabatic long range potentials and the \(|m|\)-populations are obtained from the corresponding eigenvectors. In the Appendix we show that for the \(O^{(1D_2)}\) atom only the reduced quadrupole moment \(\langle \hat{\lambda} | \hat{Q}_{(l_{\phi}=2)} \| \hat{\lambda} \rangle\) is nonzero and that it is negative. The absolute value of \(\langle \hat{\lambda} | \hat{Q}_{(l_{\phi}=2)} \| \hat{\lambda} \rangle\) does not affect the corresponding eigenvectors.

For the diatom we include the dipole, quadrupole, octupole, and hexadecapole moments \(\langle \hat{\chi} | \hat{Q}_{n,0} \| \hat{\chi} \rangle\) \(l_n = 1,2,3,4\). The values were obtained from an \textit{ab initio} calculation using the Gaussian 98 program package [35]. The NO molecule was placed along the z-axis, with the center of mass at the origin and the N atom on the positive z-axis and the NO distance equal to the experimental value of \(r_0 = 2.18\,\text{a}_0\) [36]. The two components of the \(X^2\Pi\) state were computed in a state averaged full valence complete active space self consistent field (CASSCF) calculation with an augmented correlation consistent polarized valence triple zeta (aug-cc-pVTZ) one electron basis [37]. The Gaussian package computes the Cartesian components of the multipole moments. The conversion to spherical components is straightforward as described, e.g., in Appendix E of reference [38].

The crucial assumption in the model is that upon excitation the system proceeds adiabatically on some potential surface until a critical atom-diatom separation \(R_c\) is reached, beyond which the interaction is too weak to affect the atomic polarization. This is, of course, a simplification because in reality there will be a transition region rather than a transition point between the short range adiabatic and long range diabatic regions.

Despite the numerous previous studies on the photodissociation of NO\(_2\) above the second dissociation limit described in the Introduction, it is not certain which adiabatic
Photolysis of NO$_2$ at multiple wavelengths. 

potential leads to the O($^1D_2$) product. Therefore, we will present below the results for the full range of the angle $\gamma$ for all five states included in the model.

V.4.3. Results from the semi-classical model

In the model described above there are three independent parameters for each channel: the anisotropy parameter $\beta_v$ and the relative populations $p_1 / p_0$ and $p_2 / p_0$. To find the best fit we varied $\beta_v$ from -1 to 2 in steps of 0.01 and we also varied the populations in steps of 0.01 and for each case we computed the error as

$$
\left( \frac{1}{4} \sum_{J_f=1,3} \left| I_{\text{experiment}}(J_f, J_i) - I_{\text{model}}(J_f, J_i) \right|^2 d\cos \theta \right)^{1/2}
$$

(1.16)

We include the factor of $1/4$ because the range of integration is $[-1,1]$ and two images contribute. The Legendre moments of the measured O($^1D_2$) ion images for $v=1,2,3,$ and 4 for both detection schemes are given in Table III. The anisotropy parameters $\beta_v$ and the fragment polarizations obtained from fitting these images with Eqn. (1.11) are given in Table IV. In Fig. 5 we compare the measured angular distributions with the fit. For $v=2,3,4$ we obtain good fits with the errors as defined in Eqn. (1.16) of about 0.025. As described above we determined the best fit by trying all possible values of $\beta_v$ and populations $p_m$. With this procedure we can not only determine the value of $\beta_v$ for which the total fit error is the smallest, but we also find the values of $\beta_v$ for which either the error in the $^1P_1 \leftrightarrow ^1D_2$ image or the error in the $^1F_3 \leftrightarrow ^1D_2$ is smallest.

Table III: The Legendre moments $\tilde{c}_v = c_v/c_0$ of the measured O($^1D_2$) ion images for both detection schemes.

<table>
<thead>
<tr>
<th>$v$</th>
<th>$\tilde{c}_2$</th>
<th>$\tilde{c}_4$</th>
<th>$\tilde{c}_6$</th>
<th>$\tilde{c}_2$</th>
<th>$\tilde{c}_4$</th>
<th>$\tilde{c}_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.108</td>
<td>0.922</td>
<td>0.320</td>
<td>0.565</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1.038</td>
<td>-0.222</td>
<td>-0.174</td>
<td>0.632</td>
<td>-0.046</td>
<td>-0.013</td>
</tr>
</tbody>
</table>
Table IV: The anisotropy parameters $\beta_v$ and the populations $p_m$ obtained from fitting the measured $O(\hat{D}_2)$ angular distributions with Eq. (7). The multipole moments of the density matrix $\rho_{0,PF}^{(k)}$ are related to the populations by Eq. (6). Note that $\rho_{0,PF}^{(0)} = 1/\sqrt{2J_v + 1} = 1/\sqrt{5}$.

<table>
<thead>
<tr>
<th>$v$</th>
<th>$\beta_v$</th>
<th>$p_0$</th>
<th>$p_1$</th>
<th>$p_2$</th>
<th>$p_3$</th>
<th>$p_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.28</td>
<td>0.18</td>
<td>0.82</td>
<td>0</td>
<td>-0.32</td>
<td>-0.26</td>
</tr>
<tr>
<td>2</td>
<td>0.89</td>
<td>0.35</td>
<td>0.37</td>
<td>0.28</td>
<td>-0.14</td>
<td>0.11</td>
</tr>
<tr>
<td>3</td>
<td>0.79</td>
<td>0.46</td>
<td>0.32</td>
<td>0.22</td>
<td>-0.21</td>
<td>0.20</td>
</tr>
<tr>
<td>4</td>
<td>0.38</td>
<td>0.23</td>
<td>0.39</td>
<td>0.38</td>
<td>-0.02</td>
<td>0.02</td>
</tr>
</tbody>
</table>

For $v=2,3,$ and 4 the values of $\beta_v$ obtained in this way differ by less than 0.04. For $v=1$, however, the error in the simultaneous fit is about 0.1 and the values of $\beta_1$ for which the individual images fit best differ by about 0.5. It seems that for this case at least one of the assumptions leading to Eqn. (1.11) is not valid and we will not consider the $v=1$ result further in developing the electrostatic model. The calculated multipole moments averaged over the two components of the NO($^2\Pi$) state that were used as input to the electrostatic model are given in Table V. The experimental value for the dipole moment of the ground state is $0.0158 \text{ D} = 0.00622 \text{ a.u.}$ and the $N^5O^5+$ polarity is found in all high level ab initio calculations.

Table V: Calculated multipole moments of NO($^2\Pi$) in atomic units.

<table>
<thead>
<tr>
<th>$l_A$</th>
<th>$\rho_{l_A,0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.0937</td>
</tr>
<tr>
<td>2</td>
<td>-0.8490</td>
</tr>
<tr>
<td>3</td>
<td>-0.9523</td>
</tr>
<tr>
<td>4</td>
<td>-0.6394</td>
</tr>
</tbody>
</table>
The potentials obtained by diagonalizing the interaction matrix [Eqn.(1.15)] for \( R_c=5a_0 \) are shown in Fig. 6. Note that all the potentials shown would split into an \( A' \) and an \( A'' \) potential if the \( ^3\Pi \) character of NO would be taken into account. The choice of \( R_c=5a_0 \) is rather arbitrary. We found, however, that qualitatively the shape of the potentials and the fragment polarizations derived from the model are quite insensitive to the choice of \( R_c \).

Figure 5: The experimental \( I_{\text{ion}}(\theta) \) (solid lines) for both detection schemes and the fit as described in Sec. 5 (dashed lines).
Figure 6: The adiabatic potentials obtained as the eigenvalues of the interaction matrix (Eqn. (1.15)) for $R = 5a_0$.

Figure 7: The fragment polarizations for all five states corresponding to the potentials of Fig. 6 for all values of the Jacobi angle $\gamma$. The three corners of the triangle correspond to fragments with pure $p_m = 1$ for $m=0,1,2$, and for an arbitrary point in the triangle the population $p_m$ is proportional to the distance to the side opposite to the $p_m = 1$ corner. The $A'$ states have $p_0 = 0$ and are shown on the side marked with the + signs. The solid line corresponds to the $1A'$ state, the dotted line to the $2A'$ state and the dash-dot line to the $3A'$ state. The fragment polarizations derived from the fit to the experimental images for $v=2,3$, and 4 are indicated by circles.
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For each of the five eigenvectors of the interaction matrix we obtain the relative populations $p_1 / p_0$, and $p_2 / p_0$ for each value of the Jacobi angle $\gamma = 0 - 180^\circ$. Since the sum of the populations is equal to 1 we can graphically represent the computed and measured fragment polarization as points in an equilateral triangle as shown in Fig. 7. In Fig. 8 we plot the computed $|m|$-populations as a function of the Jacobi angle $\gamma$.

Figure 8: The populations $p_m^E$ for the $A'$ and $A''$ states as a function of the Jacobi angle $\gamma$. 

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V.5. Discussion

If only the fragment polarization are considered, Fig. 7 suggests that the observed polarizations could be accounted for by dissociation on the 3A' surface. However, this state in the model corresponds to the two most repulsive states correlating with the NO(X^2Π)+O(1D_2) limit. From the limited amount of information in the literature on the states that correlate with O(1D_2) [39] it seems more likely that around 205 nm the 1A' model state is involved. In Tables II and IV (experiment and fit) we see that the v=4 channel has the lowest β parameter (0.38) and the lowest m=0 population (0.23) (ignoring the v=1 state because the fit was not good, presumably, as we have mentioned, due to the breakdown of one or more of the assumptions leading to Eqn (1.11). On kinematic grounds, a lower value of the anisotropy parameter most probably corresponds to a larger bending (and a larger angle γ). Examination of Fig. 8 shows that only for the 1A' state is p_0 a decreasing function with respect to γ (for the range 0<γ<50°, whereafter it shows a small secondary maximum at γ = 90°). Furthermore, from Fig. 7 it is clear that if we take an average over a range of angles, the 1A' curve approaches the observations for v=2,3, and 4. Averaging has no effect for the 2A' and the A" states. If more than one potential contributes to the O(1D_2) product these arguments are, of course, no longer valid.

V.6. Summary

In this paper we have presented the findings of the study concerned with the photodissociation dynamics of the NO_2 molecule in one laser experiment for both reactions (1.1, 1.2). It was found from the present work that O(1D) product using both photon resonance of both 3p^3P_1-1D_2 and 3p^3F_2-1D_2 transition is produced via 2D_2^1A_1 parallel transition. For the transition 3p^3P_1-1D_2, anisotropy parameter β was found to be 1.1 which is not in agreement with the experimental results presented by both Shafer et
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...al. [17] and Demyanenko et al. [10]. The 3p'$_1$F$_3$-$^1$D$_2$ transition product was studied for the first time and the anisotropy parameter was found 0.3 very different than the 3p'$_1$P$_1$-$^1$D$_2$ transition due to the different polarization effect at 200 nm.

Our experimental results for O(3P) channel are in good agreement with experimental results by Ahmed et al.[19]. It was necessary to keep the gas pressure and the concentration of NO$_2$ very low in order to obtain a good image resolution.

References


Appendix: \( \text{O}(^1\text{D}_2) \) quadrupole moment

In a one determinant approximation the \(|\lambda\mu\rangle\rangle_{2,2}\) state of \( \text{O}(^1\text{D}_2) \) is given by 
\[ |1s\bar{1}s2s2\bar{2}s^2p_0,2\bar{p}_0,2p_0,2\bar{p}_1, \rangle. \] Since the \( s \) orbitals do not contribute to the quadrupole moment we find that
\[
\langle 22|\hat{Q}_{2,0}|22 \rangle = 2\langle \hat{a}2p_0|\hat{Q}_{2,0}|2p_0 \rangle + 2\langle 2p_1|\hat{Q}_{2,0}|2p_1 \rangle.
\]

The angular part of the atomic integrals can be evaluated analytically and the integrals can be expressed in terms of the expectation value \( \langle r^2 \rangle \): \( \langle 2p_0|\hat{Q}_{2,0}|2p_0 \rangle = -\frac{2}{5}\langle r^2 \rangle \) and \( \langle 2p_1|\hat{Q}_{2,0}|2p_1 \rangle = \frac{1}{5}\langle r^2 \rangle \), and we find \( \langle 22|\hat{Q}_{2,0}|22 \rangle = -\frac{2}{5}\langle r^2 \rangle \). The reduced quadrupole moment is implicitly defined by the Wigner-Eckart theorem
\[
\langle \lambda\mu|\hat{Q}_{B}^{(\lambda)}|\lambda\mu \rangle = -\langle\lambda\rangle^{\lambda\mu - \lambda\mu} \langle\lambda\rangle^{\langle\lambda\rangle^{(\lambda)}|\hat{Q}_{B}^{(\lambda)}|\lambda\rangle}.
\]
Evaluating the 3-j symbol gives \( \langle \lambda\rangle^{\langle\lambda\rangle^{(\lambda)}|\hat{Q}_{B}^{(\lambda)}|\lambda\rangle} = -\sqrt{\frac{14}{5}} \langle r^2 \rangle \), and so it must be negative.
Summary

This thesis presents the results of a dynamical study of NO₂ (nitrogen dioxide) and Tetrakis (dimethylaminoethylene) molecules using intense laser light. Under high energy excitation the molecules can only be ionized, excited or dissociated (i.e. be broken into fragments). When a molecule (or atom) interacts with a photon of sufficient energy then ionization may occur through removal of an electron. As the ionization potential of the smallest molecules is above 8 eV, highly energetic photons are required to induce ionization through one-photon absorption. Single photon ionization requires a short wavelength photon (λ < 150 nm), which is currently difficult to achieve in the laboratory. However, ionization can also be achieved using multiple photons of a longer wavelength which can be produced by pulsed laser beams. Therefore, the use of laser light for multiphoton ionization (MPI) has become a standard technique for producing ionized states.

The technique of mapping the distribution of the various component elements (ions, electrons) over an extended area of a solid sample, with high spatial resolution is presented in this thesis, where the technique is commonly known as Velocity Map Imaging. The ions or electrons are detected at the end of a 34 cm flight tube by an imaging detector (MCP-phosphor screen assembly). Images are collected with a CCD camera and archived using a data acquisition system. An electronic device is used to measure ion arrival times in order to direct the gating of the MCP and to provide mass spectra. Careful analysis of the ion images provides information on the speed, angular distribution of the fragments, the energy partitioning, excited state lifetime, product quantum yields, and nature of the excited state.

For the studies presented in this thesis both nanosecond and femtosecond laser beams have been used. Nanosecond laser pulses provide a narrow band of frequencies and can excite only one or few ro-vibrational states. Due to its characteristics, the nanosecond laser pulse is a good candidate for studying the electronic, vibrational and rotational structures of molecules. For the energy resolution experiment (ns laser pulse) a Resonant Enhanced
Multiphoton Ionization (REMPI) technique was used in order to study neutral excited states by promoting ionization via ro-vibrational levels of a given electronic state. The ionization process is greatly enhanced if this excited state is resonant at the energy of one or two absorbed photons.

As the laser pulse is shorter in length (i.e. $10^{-12}$ s$^{-1}$) the laser bandwidth is converted into a wide spectrum of frequencies i.e. an ultrashort laser pulse will excite an ensemble of ro-vibrational levels instead of one single level. Therefore, the femtosecond laser pulse has the advantage of being able to detect very short lived states which exist in excited molecules.

The ionization induced by the intense laser radiation offers some advantages for studying the dynamics of ultrafast chemical reactions in femtosecond pump-probe experiments. For Tetrakis, we probed the parent molecule immediately after the molecule was electronically excited and subsequently monitored the electrons released as a result of the excitation. The kinetic energy of the electrons provides information about the properties of the parent molecule when it was ionized. For the pump-probe experiment we can monitor also the ions: any electronically excited state of the molecule is expected to give an enhanced ion signal depending on its ionization potential. The ionization could be followed by fragmentation, which provides additional information on transient intermediate states and/or species. Monitoring the kinetics of the parent and various fragment ions/electrons in a pump-probe delay experiment, we are able to follow the molecule from state to state all along the primary photochemical reaction path, which is often completed within few hundreds of femtoseconds.

The Velocity Map Imaging in conjunction with pump-probe delay technique is a powerful tool in spectroscopy. We used this tool in order to take photoelectron images of the Tetrakis molecule as described in Chapter III. The electrons spectra behind the images reveals the existence of a short lived Rydberg state (~ 400fs) localized between ground and excited Valence state of the Tetrakis molecule. Moreover, the same tool was also used in
Chapter IV for describing mechanisms underneath of triatomic NO$_2$ molecule. The ions spectra reveal not only kinetics but also oscillations of wave-packet motion which measure the energy spacing between the resonant levels of two states ($\tilde{A}^2B_2/\tilde{X}^2A_1$).

Chapter V presents the findings of the study concerned with the photodissociation dynamics of the NO$_2$ molecule in one nanosecond laser experiment using REMPI in conjunction with the Velocity Map Imaging technique (VMI). Detailed information on the electronic angular momentum alignment of the $^1D_2$ state is obtained from analysis of the polarization sensitivity of the O($^1D$) images using the two resonant intermediate states: $3p^4P_1$.
Samenvatting

In dit proefschrift staan de resultaten beschreven van dynamische studies aan NO₂ (stikstofdioxide) en Tetrakis (dimethylaminoethyleen), gebruik makend van intens laserlicht. Bij hoogenergetische excitatie kunnen moleculen alleen worden geëxciteerd, geïoniseerd, of gedissocieerd (d.w.z. in stukken gebroken). Wanneer een molecuul of atoom wisselwerkt met een foton van voldoende grote energie, kan ionisatie optreden door de verwijdering van een elektron. Omdat de ionisatiepotentiaal van de kleinste moleculen boven de 8 eV ligt, zijn zeer hoogenergetische fotonen nodig voor ionisatie via één-foton absorptie. Dit proces vereist een foton met een korte golflengte (λ < 150 nm), wat op het moment moeilijk te realiseren is in het laboratorium. Ionisatie kan echter ook bereikt worden door middel van absorptie van meerdere fotonen met langere golflengte, geproduceerd door gepulste lasers. Daarom is het gebruik van laserlicht voor multifoton-ionisatie (MPI) een standaardtechniek geworden voor de productie van geïoniseerde toestanden.

De techniek van het afbeelden van de verdeling van de verschillende elementen (ionen, elektronen) van een vaste-stof monster, over een uitgebreid gebied met hoge ruimtelijke resolutie, wordt in dit proefschrift beschreven. Deze techniek staat in het algemeen bekend als Velocity Map Imaging. De ionen of elektronen worden gedetecteerd door een MCP-fosforscherm opstelling aan het eind van een vluchtbuis van 34 cm. De beelden worden opgenomen met een CCD-camera en opgeslagen met behulp van een data-acquisitie systeem. De aankomsttijden van de ionen worden gedetecteerd voor de triggering van de MCP en om massaspectra te meten. Zorgvuldige analyse van de ionenbeelden levert informatie op over de snelheid en hoekverdeling van de brokstukken, de energieverdeling, en de aard en de levensduur van de aangeslagen toestand.

Voor het in dit proefschrift beschreven onderzoek zijn zowel nanoseconde- als femtoseconde-gepulste lasers gebruikt. Nanoseconde laserpulsen hebben een relatief smalle bandbreedte en kunnen daardoor alleen één of enkele ro-vibrationele toestanden aanslaan.
Vanwege deze eigenschappen is de nanosecondenlaser een goed instrument voor het bestuderen van de elektronische, vibrationele en rotationele structuren van moleculen. Voor het energie-resolutie experiment (ns laserpuls) is de “resonant versterkte multifoton ionisatie” techniek (REMPI) gebruikt om neutrale aangeslagen toestanden te bestuderen, door ionisatie te bevorderen via ro-vibrationele niveaus van een gegeven elektronische toestand. Het ionisatieproces wordt zeer versterkt als deze aangeslagen toestand resonant is bij de energie van een of twee geabsorbeerde fotonen.

Bij kortere laserpulsen ($10^{-12}$ s$^{-1}$) wordt de bandbreedte omgezet in een breed frequentiespectrum. Een zeer korte laserpuls zal dus een aantal ro-vibrationele niveaus aanslaan in plaats van één enkel niveau. De femtosecondenlaser kan daardoor gebruikt worden voor het detecteren van zeer kort levende toestanden die voorkomen in aangeslagen moleculen.

Ionisatie ten gevolge van intense laserstraling biedt enkele voordelen voor de bestudering van de dynamica van ultrasnelle chemische reacties in femtoseconde pump-probe experimenten. Voor Tetrakis hebben we het moedermolecuul gemeten onmiddellijk nadat het molecuul elektronisch was aangeslagen, en vervolgens de elektronen gevolgd die vrij kwamen als gevolg van de excitatie. De kinetische energie van de elektronen geeft informatie over de eigenschappen van het moedermolecuul toen het aangeslagen was. Voor het pump-probe experiment kunnen we ook de ionen volgen: elke elektronisch aangeslagen toestand van het molecuul geeft naar verwachting een versterkt ion-signal afhankelijk van zijn ionisatiepotentiaal. De ionisatie kan gevolgd worden door fragmentatie, wat extra informatie oplevert over vervallende tussentoestanden en/of -soorten. Door de kinetica van het moedermolecuul en de verschillende ion/elektronfragmenten te volgen in een pump-probe experiment met vertraging, zijn we in staat om het molecuul van toestand tot toestand te volgen langs het hele primaire fotochemische reactiepad, dat vaak wordt afgelegd binnen een paar honderd femtoseconden.
De combinatie van Velocity Map Imaging en de pump-probe techniek is een krachtige techniek in de spectroscopie. Wij hebben deze techniek gebruikt voor de bestudering van het Tetrakis molecuul zoals beschreven in hoofdstuk III. De elektronspectra tonen het bestaan van een kortlevende (~ 400 fs) Rydberg toestand aan tussen de grond- en aangeslagen toestand van het Tetrakis molecuul. Dezelfde techniek is gebruikt om de mechanismen van het NO$_2$-molecuul te beschrijven, zoals uitgelegd in hoofdstuk IV. De ionspectra laten niet alleen de kinetica maar ook de oscillaties van de golfpakketbeweging zien, een maat voor het energieverschil tussen de resonante niveaus van de twee toestanden $\tilde{\text{A}}^2\text{B}_2^\alpha / \tilde{\text{X}}^2\text{A}_1$.

In hoofdstuk V worden de resultaten gepresenteerd van een studie naar de fotodissociatie-dynamica van het NO$_2$ molecuul met een combinatie van REMPI en VMI. Gedetailleerde informatie over het elektronisch hoekmoment van de $^1\text{D}_2$-toestand is verkregen door de analyse van O($^1\text{D}$) beelden die de polarisatiegevoeligheid weergeven, gebruikmakend van twee resonante tussentoestanden: $3p'\text{P}_1$ en $3p'\text{F}_3$. 
Acknowledgment

I would like to acknowledge the support and encouragement of my supervisor, prof. dr. D. H. Parker, for getting me involved with this project, helping me through it, bouncing ideas and for the help in writing this thesis.

I would also like to thank the other senior academic staff not only from the Department Molecular and Laser Physics, but also from other institutions throughout Europe, namely: dr. W.L. Meerts, dr. G. Groeneboom, prof. J. Reuss, dr. A. Baklanov, prof. dr. B. J. Whitaker, dr. B. Soep, prof. the assistance given generally always causes relief of some despair. Moreover, I would also like to thank my work colleagues from the Molecular and Laser Physics Department for their support which was also very much appreciated. Specifically, I acknowledge A. Eppink, S. Min Wu (Malcom), R. Cireasa, A. Moise, I. Garcia, D. Radenovic, D. Chestakov, K. Vidma, H. Naus.

The technical staff has also been very friendly and helpful in dealing with any practical problems that came up during the course of the experimental work. I am always thinking that such a large experimental department would less efficiently if it were not for the support of all of the technical staff. I am particularly grateful to those people who were more directly involved with my experiments, namely: L. Gerritsen and E. van Leeuwen. I also thank the very efficient electronically technician P. Claus who works for the entire department and who has been very helpful and speedy in making or modifying things and having great patience. I also wish to thank the support of the other technical staff: A. van Roij and C. Sikkens, and also the secretarial department, especially to Erna Gouvens who managed to find for me a decent and convenient accommodation.

A part of my work was conducted at the SACLAY research institute, situated outside Paris. Therefore, I would like to gives a special thank you to the Saclay group for the
friendly working environment and kindness shown during my visits to their laboratory: B. Soep, E. Gluoagen, S. Sorgues, J. P. Visticot, and J. M. Mestdagh.

Last but in no means least, I would like to thank to people in the university, connected more or less with my research work, ‘the romanian clan’ who ease my homesickness, friendship made over four years of being here: Raluca, Angela, Angelica, Miruna & Bram, Simona & Sacco, Gabi, Cristina, Afric, Gowri. All those people who came and went: Nico&Lulu, Iulia & Marius, Ivan, Rogir, Reijer.

Multumesc familiei mele si tuturor celor de acasa pentru toata dragostea si incurajarile prinate pe toata perioda acestui proiect.

I thank my boyfriend Jason for all the love and support and for helping me to improve my English.

Angela Marcela Coroiu, August 12, 2005
List of publications


