Kirsten Schnorr

XUV Pump-Probe Experiments on Diatomic Molecules

Tracing the Dynamics of Electron Rearrangement and Interatomic Coulombic Decay

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Tracing the Dynamics
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Doctoral Thesis accepted by
the University of Heidelberg, Germany

🐎 Springer

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Supervisor's Foreword

The advent of free-electron lasers (FELs) has opened up entirely new research opportunities by combining the key features of optical lasers, such as short and intense pulses, with those of synchrotron sources, which routinely deliver extreme-ultraviolet (XUV) and X-ray radiation. In this thesis, the first FEL that reached into the XUV, the free-electron laser in Hamburg (FLASH), has been employed to investigate fundamental relaxation mechanisms of excited molecules in the time domain.

The short pulse-durations in combination with high intensities allow XUV-pump–XUV-probe experiments to be performed: The first laser pulse ionizes a molecule, thereby initiating a certain reaction and a delayed copy of the first pulse probes the transient state by further ionizing the molecular ion. The pump–probe technique was combined with multi-particle coincidence spectroscopy by using a so-called reaction microscope to investigate electron transfer in dissociating multiply charged iodine molecules and to determine the lifetime of interatomic Coulombic decay (ICD) in neon dimers.

Electron transfer is a ubiquitous relaxation process in plasma physics, chemical reactions, and ion collisions, in particular for slowly moving nuclei. This energy regime is challenging for theory and experimentally difficult to access. However, this thesis presents an elegant way to study and control electron transfer between two dissociating iodine ions by combining the pump–probe technique with Coulomb explosion imaging. The obtained results are in excellent agreement with the intuitive over the barrier model, which is commonly used in slow ion-atom collisions.

Due to the high FEL intensities, charge states up to I_2^{17+} were reached upon impact of a single 87 eV pulse. Understanding the fragmentation dynamics of multiply ionized molecules, in particular those with heavy constituents serving as photoabsorption centers, is of crucial importance for the realization of single particle imaging at FELs. This technique is only possible if the molecule is imaged before it is damaged. Therefore, the present prototype study gives precious input on

how efficiently and over which distances electrons are transferred in multiply charged molecules.

In ICD, a highly excited atom or ion transfers its excess energy radiationless over quite large distances to one of its neighbors, which is consequently ionized. This process occurs in weakly bound systems, like van der Waals and hydrogen bonded clusters, and happens on timescales that are typically two to three orders of magnitude shorter than competing relaxation mechanisms. The ejection of slow electrons together with the aforementioned key features make ICD an important contributor to radiation-induced DNA damage in tissue, with far reaching consequences for cancer therapy. Since the prediction of ICD in 1997, it has triggered a large amount of theoretical and experimental effort; however, no direct time-resolved measurement of the quintessential lifetime had been performed until now. Within this thesis an XUV pump-probe scheme was applied to determine the ICD lifetime in neon dimers, resulting in a value of 150 ± 50 fs, which agrees well with calculations, provided nuclear motion is explicitly taken into account.

Heidelberg, August 2014   Priv.-Doz. Dr. Robert Moshammer

Abstract

Within this thesis the dynamics of diatomic molecules, initiated and probed by intense extreme-ultraviolet (XUV) radiation delivered by the free-electron laser in Hamburg (FLASH), is investigated by means of three-dimensional recoil-ion momentum spectroscopy.

In a study on iodine molecules I_2, ultrafast charge rearrangement between the two ions of a dissociating molecule is triggered by the localized absorption of short 87 eV XUV pulses at either of the ions and studied as a function of their internuclear distance. This yields the critical distance and the corresponding time up to which charge transfer along the internuclear axis can take place dependent on the charge state of the photon-absorbing ion. Additionally, the response to intense XUV radiation of molecules and of isolated atoms is compared, yielding that higher charge states are reached for the latter.

The lifetime of interatomic Coulombic decay (ICD), an efficient relaxation mechanism in weakly bound systems, is determined for the $(2s^{-1})$ inner-valence vacancy of the neon dimer Ne_2. Applying an XUV pump-probe scheme at a photon energy of 58 eV, the dynamics of ICD is for the first time traced directly. The measured lifetime of 150 ± 50 fs only agrees well with predictions that explicitly take nuclear dynamics prior to the decay into account, demonstrating the key role of the motion for ICD in light systems.

Contents

Chapter 1
Introduction

Molecules undergoing a chemical reaction, such as dissociation or ionization, are essentially few-particle quantum systems that dynamically evolve as a function of time. They progress from an initial to a final state, passing through—quite often very short lived—intermediate states. While the study of the initial and the final state can provide some aspects, such as lifetimes and state populations, a deeper insight into the dynamical properties calls for the investigation of the intermediate states. This is the subject of femtochemistry, which aims to study the formation and breaking of chemical bonds on their natural time and length scales [71]: the femtosecond (10^{-15}s) and the Ångström (10^{-10}m). It requires dedicated time-dependent methods, capable of isolating each intermediate state temporally and determining their essential features.

The most prominent experimental technique for tracing the real-time evolution of photo-induced processes is pump-probe spectroscopy [72]. A first light pulse initiates a reaction in the system of interest, which is then followed in time by probing the system's state with a second light pulse at variable time delay. The resolvable time scales are on the order of the pulse duration, limiting the range and nature of dynamical processes that can be explored. Thus, in order to trace vibrational and dissociative motion in molecules, which occur within tens to hundreds of femtoseconds, pulses of corresponding duration are required. The production of such pulses became possible with advances in laser technology, in particular by the development of the mode-locking technique [23]. This method has quickly developed due to the use of Titanium:Sapphire lasers that deliver pulses with a duration in the femtosecond regime at near infrared (IR) wavelengths ($\sim$800 nm) [66]. Thus, they allow the resolution of even the fastest vibrations in small molecules [18, 22].

Nuclear motion in molecules is usually quantum mechanically treated within the Born–Oppenheimer approximation [8], which neglects coupling between electronic and nuclear motion as the former is typically a factor of thousand faster than the latter. In this estimate the potential energy of the molecule is represented by potential energy surfaces, which for diatomic molecules simplify to potential energy curves and are thus only dependent on the internuclear distance of the two nuclei. The nuclear dynamics within a molecule is described by nuclear wave packets evolving
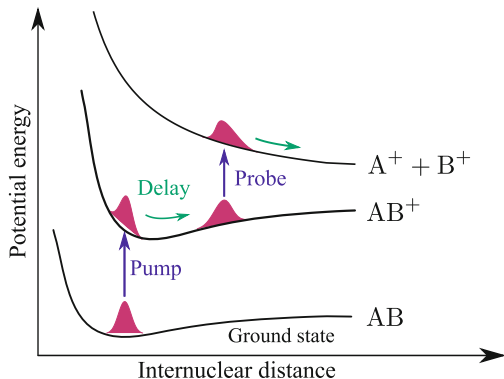
Fig. 1.1 Illustration of the pump-probe technique in a diatomic dummy molecule AB. The molecule is ionized by the pump pulse leading to the formation of a nuclear wave-packet that evolves in time in a bound electronic state of AB^+. After an adjustable time delay the probe pulse further ionizes the molecular ion leading to the population of a repulsive state resulting in a Coulomb explosion into the fragments A^+ and B^+

in time, as illustrated in Fig. 1.1: The ionization of a molecule by the pump pulse may initiate wave-packet dynamics in an intermediate electronic state due to the coherent superposition of vibrational levels. This leads to a modulated nuclear wave packet propagating along the internuclear coordinates. Probing the time evolution of the wave packet is thus equivalent to tracing the motion of the nuclei. If the probe pulse further ionizes the molecule onto a repulsive Coulomb curve, Coulomb-explosion imaging (CEI) [65] allows to access the molecular geometry by exploiting the repulsion of the quickly ionized heavy constituents. A more detailed discussion on how the interaction of light with atoms and molecules can be treated theoretically, is given in Chap. 2.

Ionization with IR lasers typically requires the simultaneous absorption of a large number of photons and thus the application of intense pulses. However, the thereby induced strong electromagnetic fields disturb the studied systems and the ongoing dynamics [15]. In order to return to the perturbative regime of single or few photon absorption, while still being able to ionize a molecule, one has to apply higher photon energies, such as that of extreme ultraviolet (XUV) radiation. Developments in recent years have yielded two different types of XUV sources capable of producing the necessary short pulses:

- High harmonic generation (HHG) sources [38, 48],
- Free-electron lasers (FELs) [7].

Each of them has its advantages and drawbacks, depending on the goal of the specific pump-probe experiment.

As HHG allows the generation of XUV and soft X-ray pulses with durations below 100 as and a fixed phase relation to the fundamental pulses [73], it enables experiments with unprecedented temporal resolution. Applying XUV-IR streaking techniques [33], delays in photoemission of tens of attoseconds [61] as well as Auger

lifetimes of a few femtoseconds [16] could be determined. Recent improvement of HHG sources has led to intensities higher than $10^{13}\frac{W}{cm^2}$ [41], which are sufficient to perform XUV pump-probe experiments. However, these intensities are not yet routinely available and they are still not high enough for inducing non-linear processes. Therefore, XUV pump-probe experiments are predominantly performed at FELs [31, 32], which deliver intensities up to $10^{18}\frac{W}{cm^2}$ [10].

FELs are able to produce coherent radiation ranging from the XUV to the hard X-ray regime with pulse durations in the order of ten femtoseconds and peak brilliances up to 8 orders of magnitude larger than that of the most powerful synchrotrons [50]. The pulses consist of stochastic spikes [1] of a few femtoseconds width that corresponds to the temporal coherence length [42]. FELs have opened up a whole new research area, as they combine the key features of lasers, such as short and intense pulses, with those of synchrotron sources delivering XUV and X-ray radiation. Before the advances in FEL technology, dynamical and non-linear studies could only be carried out with ultra-short pulses in the optical and IR regime, while inner-valence and core ionization investigations were limited to the single-photon regime by using picosecond synchrotron pulses. The first FEL that reached into the XUV regime, the free-electron laser in Hamburg (FLASH) [21], became operational in 2005, and the first hard X-ray FEL, the linac coherent light source (LCLS) in Stanford followed in 2009 [17]. At the moment, two further XUV FELs, one in Italy (FERMI) [2] and one in Japan (SCSS) [63], are available. Another hard X-ray FEL (SACLA) [29] became recently operational in Japan. Still some more are to come in the next few years, such as the European XFEL [25] in Hamburg and the SwissFEL [47] in Villigen. A basic introduction in the underlying operation principles of an FEL is given in Chap. 3.

One of the most far reaching visions for the application of FEL radiation is the imaging of single biomolecules with intense femtosecond X-ray pulses [40, 62]. By using X-ray diffraction the electron density and thus the structure of molecules can be reconstructed, which is crucial for the understanding of the functionality of biomolecules. Such studies have been performed for many years at synchrotrons and yielded hundred thousands of molecular structures so far [11]. However, the method requires large crystallized samples that for most molecules are often very difficult or even impossible to produce [13]. The intense coherent radiation of FELs with pulse durations in the femtosecond regime enables imaging of much smaller crystals (nano-crystals) [6]. Recently, the first so far unknown molecular structure, namely the *Trypanosoma brucei* enzyme, could be extracted from an experiment at LCLS [34].

Molecular imaging relies on the so-called *diffract before destroy* concept [43], where a snapshot of a structure is taken before it had time to change. Once a sample is irradiated with intense X-ray radiation, its electron density distribution and consequently the structure is modified, i.e., the molecule suffers damage. Therefore, the central question arises how fast the structural rearrangement takes place and thus whether the damage hinders the imaging of single biomolecules. Recent experiments on nano-crystallized lysozyme have shown signatures of radiation damage from X-ray pulses as short as 70 fs [39]. Photon absorption within molecules is strongly

localized at constituents with high atomic number, often having more than an order-of-magnitude larger cross sections than H or C atoms [69]. Therefore, it is crucial to understand the underlying ultrafast dynamics in order to develop improved damage models that take the spatio-temporal spread of the induced damage into account.

Localized photoabsorption efficiently triggers nuclear motion and electronic rearrangement across the entire molecule, mainly leading to its fragmentation. The induced rearrangement for few femtosecond pulses has been investigated in a recent study on methyl- and ethylselenol, both containing a heavy selenium atom as photoabsorption center [19, 20]. It could be concluded that even inside pulses as short as 5 fs ultrafast charge rearrangement took place and that it was accompanied by considerable displacement of the constituents. However, the essential questions about the time and length scales of the rearrangement remained open. This question is addressed in this thesis in the form of a pump-probe experiment on a diatomic model system, the iodine molecule I_2, with the goal to gain time resolution for the aforementioned charge rearrangement and the accompanied nuclear motion [59, 60]. In particular, the internuclear separation at which charge transfer is not possible anymore is investigated. I_2 is a well-suited target system, as it features a large cross section for the removal of inner-valence electrons around a photon energy of 90 eV [14]. Earlier studies have already explored the dissociation dynamics of molecular iodine ions [35, 36], however only for charge states up to I_2^{5+}. We reach considerably higher charge states and in addition investigate whether the highest charge states are reached for the molecule or separated iodine atoms. The production of these highly charged ions requires the absorption of multiple photons: It takes place via sequences of single-photon absorption and from some point on several photons must be absorbed simultaneously to remove further electrons [26, 51]. Investigating the pathways of multiple ionization is important to gain insight into the fundamental processes occurring when intense FEL radiation interacts with matter. The first studies of that kind were carried out in the XUV wavelength regime on Xe clusters and atoms [49, 68] and were later extended into the X-ray regime [28, 52, 70].

A completely different situation arises, when weakly bound complexes are studied. The aforementioned electron transfer, induced by the localized absorption of high energetic photons, occurs only up to a certain internuclear distance. Hydrogen bonds, which are ubiquitously contained in large biomolecules, are often so weak that the distance between the constituents are too large for electron transfer, even at equilibrium internuclear distances. If this is the case, excited species within the molecule relax by transferring their excess energy solely through the Coulomb force. An example for such a process is the Förster resonant energy transfer (FRET) between molecules, which enables for instance the light harvesting in photosynthesis [24]. Another process of this type is interatomic or intermolecular Coulombic decay (ICD) [12] taking place in weakly bound van-der-Waals and hydrogen bound clusters. Here, an excited monomer ion relaxes by transferring its excess energy to a neighboring atom or molecule, which consequently emits an electron. ICD is an extremely efficient relaxation process and ubiquitous in different chemical environments like clusters [55], He droplets [37], fullerenes [5] and aqueous solutions [45]. The ejected ICD electrons usually have low energies and therefore destroy efficiently

chemical bonds in close-by molecules [9]. Therefore ICD is expected to affect the DNA damage in radiation tumor therapy [27].

ICD occurs on time-scales of a few femtoseconds up to nanoseconds [74], depending on the system and the type of decay mechanism. From a quantum dynamical point of view, ICD and its related phenomena allow to study processes in the interesting regime where electronic transitions couple strongly to nuclear degrees of freedom. For large internuclear distances R the ICD rate is proportional to $\sim R^{-6}$ [56]. For smaller distances other decay pathways may open up, resulting in shorter lifetimes [4]. Thus, if the decaying system is given time to change its internuclear distance, the decay rate will change significantly [54, 57]. For a decay occurring within a few femtoseconds, the accompanying nuclear motion is negligible [5, 30, 44]. In contrast, it plays a crucial role for relaxation times larger than that [54]. Therefore the ICD lifetime is a crucial parameter for understanding the complex interplay between electronic and nuclear motion.

The first ICD lifetime determination in large neon clusters yielded 6 fs for $Ne^+(2s^{-1})$ ions from the bulk [44]. It neglected nuclear motion prior to the decay, which is justified because of the fast decay and the slow nuclear dynamics in the cluster. In contrast for dimers like Ne_2, lifetimes of 64–92 fs (for fixed $R = 3.2$ Å) are theoretically predicted [3, 53, 67], which are long enough to allow significant nuclear movement prior to the decay. Therefore, different experimental techniques capable of including intramolecular dynamics are required. Moreover, the calculation of distance dependent ICD decay rates is a demanding task and a recent study on NeAr showed that theory had clearly overestimated the decay width [46]. Therefore, experimentally determined lifetimes are urgently needed to benchmark theory. In the scope of this thesis the first direct time-resolved measurement of an ICD lifetime was performed by means of an XUV pump-probe scheme applied to the $(2s^{-1})$ vacancy in Ne_2 [58].

Both experiments presented in this thesis are performed applying recoil-ion momentum spectroscopy by means of a reaction microscope (REMI) [64], which was especially designed for experiments at FELs. It enables the determination of the ion momentum vectors and thus, by momentum conservation, an unambiguous identification of the fragment pairs that emerged from the same molecule. A detailed description of the operation principle of a REMI including all relevant components of the setup are given in Chap. 4.

This thesis is organized as follows: Chap. 2 begins with a theoretical description of single-electron atoms in an electromagnetic field. This is followed by a discussion of many-electron atoms and molecules. Then, the relevant relaxation processes initiated by XUV radiation are introduced with special emphasis on ICD. The basic operation principle of an FEL and the resulting characteristic radiation are introduced in Chap. 3. The experimental setup with its core, the REMI, is presented in Chap. 4, including the actual setups of the I_2 and the Ne_2 experiments. In Chap. 5 the analysis of the recorded data is discussed and the relevant observables for the interpretation of the data are introduced. The results for the I_2 experiment are presented in Chap. 6 and the ICD lifetime determination in Chap. 7. In the final Chap. 8 we conclude with a summary of the obtained results.

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Chapter 2
Photoionization and Interatomic Coulombic Decay

The type of process that may be induced in an atom by the interaction with a single photon is strongly dependent on the photon energy. An overview of the energy regimes in the electromagnetic spectrum is given in Fig. 2.1. For wavelengths in the infrared (IR) and optical regime, electron-photon interaction is dominated by elastic Rayleigh scattering. For ultraviolet (UV) radiation and X-rays up to a few keV, inelastic photoabsorption is the most relevant process. For even higher photon energies, Compton scattering becomes dominant and is eventually taken over by pair creation when the energy increases further. Throughout this thesis we will mostly address the interaction of extreme ultraviolet radiation (XUV), corresponding to the energy regime of $10\,\mathrm{eV} < h\nu < 124\,\mathrm{eV}$, with atoms and molecules, which usually leads to photoionization.

The absorption of a single and of multiple photons in a one-electron system is introduced in Sect. 2.1. For the description of a system consisting of more than just a core and an electron, the electron-electron interaction must be taken into account. Common techniques and approximations used to describe the Coulomb repulsion between the electrons and the electron correlation for atoms and molecules are presented in Sect. 2.2. The cross sections for the absorption of single XUV photons are discussed in Sect. 2.3. As high energetic photons efficiently remove inner-shell and core electrons, highly excited ions are often created. The most relevant relaxation mechanisms are explained in Sect. 2.4. One particular relaxation mechanism, interatomic Coulombic decay (ICD), which relies on the Coulomb interaction of a highly excited monomer with its environment, is presented in Sect. 2.5. A classical simulation for pump-probe schemes, which is applied to extract time-information for such molecular processes, is presented in Sect. 2.6. The chapter concludes with a model for charge transfer in dissociating molecules in Sect. 2.7.