## Investigating Ultrafast Nanoscale Surface Dynamics using Reaction Nanoscopy

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### Zusammenfassung

Die Photochemie, die Erforschung lichtinduzierter chemischer Reaktionen, spielt eine entscheidende Rolle bei zahlreichen natürlichen und synthetischen Prozessen, einschließlich der Photosynthese und der Umwandlung von Sonnenenergie. Während Entwicklungen in der Nanotechnologie und der Lasertechnik zu bemerkenswerten Fortschritten in der Photochemie geführt haben, bleiben Untersuchungen des dynamischen Verhaltens von Materialien auf der Nanoskala aufgrund der beteiligten Längen- und Zeitskalen eine Herausforderung. In dieser Arbeit wird die Reaktions-Nanoskopie eingesetzt, um diese Herausforderung zu meistern, und neue Möglichkeiten zur Beobachtung von Reaktionen im Nanomaßstab aufgezeigt. Die Reaktionsnanoskopie nutzt die dreidimensionale Ionenimpulsspektroskopie und ermöglicht dadurch eine umfassende Untersuchung der Energie- und Impulsverteilung von Ionen, die während laserinduzierter Reaktionen von der Oberfläche von Nanopartikeln abgegeben werden.

Die Fähigkeit von Nanopartikeln, elektromagnetische Felder zu lokalisieren und zu verstärken, ist von entscheidender Bedeutung für die Beeinflussung von Oberflächenreaktionen auf der Nanoskala. Während frühere Forschungen das laserinduzierte Brechen und Bilden von Bindungen auf Nanopartikeloberflächen beobachtet haben, ist die optische Kontrolle von Nahfeld-vermittelten Oberflächenreaktionen im Nanobereich schwer zu erreichen. Die vorliegende Arbeit schließt diese Lücke, indem sie die erste experimentelle Demonstration der rein optischen, nanoskopischen räumlichen Kontrolle molekularer Reaktionsausbeuten auf isolierten Siliziumdioxid-Nanopartikeln vorstellt. Durch die Anpassung von Nahfeldern mit wellenformgesteuerten linearen und bizirkularen Zweifarben-Laserpulsen und den Einsatz von Reaktions-Nanoskopie wird gezeigt, dass der Entstehungsort von Molekülfragmenten auf der Oberfläche von Nanopartikeln mit einer Winkelauflösung von etwa 8° bestimmt werden kann. Dies entspricht einer räumlichen Auflösung von etwa 20 nm für 300 nm Siliziumdioxid-Nanopartikel. Insbesondere wird eine ortsselektive Protonenemission aus der dissoziativen Ionisierung von adsorbierten Molekülen beobachtet, die von der Polarisation und der relativen Phase der Zweifarbenpulse abhängt. Die Ergebnisse werden durch klassische Trajektorien-Monte-Carlo-Simulationen bestätigt, die auf starker Feldionisation in Nahfeldern und quasi-statischen Ladungswechselwirkungen basieren.

Der zweite Teil der Arbeit ist eine Weiterentwicklung der vorangegangenen Arbeiten zur räumlichen und zeitlichen Verfolgung der Reaktionsprodukte mit einer bisher unerreichten räumlichen und zeitlichen Auflösung im Nanometer- und Femtosekundenbereich. Sie demonstriert die erste Realisierung der Pump-Probe-Reaktions-Nanoskopie zur Untersuchung der Oberflächenladungsdynamik in einzelnen Siliziumdioxid-Nanopartikeln. Die Studie untersucht den Prozess der Oberflächenladungsrelaxation und seine Auswirkungen auf die Bindungsschwächung der adsorbierten Molekülgruppen auf einzelnen Siliziumdioxid-Nanopartikeln. Die Studie bietet eine vierdimensionale Visualisierung der Oberflächenladungsdichte. Sie ermöglicht die Unterscheidung der Beiträge des zugrundeliegenden physikalischen Prozesses, der aus Diffusion und Ladungsverlust auf verschiedenen Zeitskalen besteht, unterstützt durch semiklassische Simulationen. Die Simulationen geben Aufschluss über die Rolle der laserinduzierten Oberflächenladungen bei der Schwächung der terminalen O-H-Bindungen an der Grenzfläche, deren Dynamik durch die Umverteilung von anfangs lokalisierten Ladungsträgern verursacht wird.

Im letzten Teil der Arbeit wird eine Studie vorgestellt, die sich auf die Bildung von Trihydrogenkationen auf der Oberfläche von stark feldbestrahlten Goldnanopartikeln mit Citrat-Oberfläche konzentriert. Die Studie verdeutlicht, wie Formvariationen die Reaktionslandschaft der Nanopartikeloberfläche verändern können, indem sie die Reaktionsprodukte vergleicht, die von stark feldionisierten kugelförmigen und facettierten Goldnanopartikeln abgegeben werden. Die Untersuchungen unterstreichen die bedeutende Rolle der Ladungslokalisierung bei der Steuerung der Reaktionsdynamik, wobei sterische Effekte zur allgemeinen Steigerung der Reaktivität beitragen. Es wird gezeigt, dass facettierte Goldnanopartikel durch die Ausnutzung der protonenreichen Umgebung, die durch die laserinduzierte Ionisierung der Nanopartikeloberfläche entsteht, eine erhöhte katalytische Aktivität aufweisen, was ihr Potenzial für verschiedene chemische Umwandlungen hervorhebt. Insgesamt erforscht diese Arbeit die ultraschnelle Oberflächendynamik im Nanomaßstab, die eine rein optische räumliche Kontrolle über nanoskopische Reaktionsausbeuten umfasst, und enthüllt die vierdimensionale Oberflächenladungsdynamik auf Nanopartikeln, die Auswirkung von Oberflächenladungen auf die Bindungsschwächung und die Aufdeckung morphologieabhängiger Effekte auf die Modulation des katalytischen Verhaltens von Goldnanopartikeln. Die Fähigkeit, Oberflächenreaktionen auf Nanopartikeln zu kontrollieren und zu analysieren, ebnet den Weg für Fortschritte in der Photokatalyse, der Atmosphärenchemie und anderen Bereichen, in denen diese grundlegenden Prozesse eine Rolle spielen.

### Abstract

Photochemistry, the study of light-induced chemical reactions, plays a crucial role in numerous natural and synthetic processes, including photosynthesis and solar energy conversion. While advancements in nanotechnology and laser technology have fueled remarkable progress in photochemistry, understanding the dynamic behavior of materials at the nanoscale remains challenging due to the involved length and time scales. This thesis employs reaction nanoscopy to address this challenge that goes beyond the abilities of existing techniques in observing reactions occurring at the nanoscale. Reaction nanoscopy utilizes three-dimensional ion momentum spectroscopy and enables a comprehensive investigation of the energy and momentum distribution of ions emitted from the nanoparticle surface during laser-induced reactions.

The ability of nanoparticles to localize and enhance electric fields is crucial for manipulating surface reactions at the nanoscale. While previous research has observed laserinduced bond-breaking and formation on nanoparticle surfaces, achieving nanoscale optical control of near-field-mediated surface reactions has remained elusive. This thesis bridges this gap by presenting the first experimental demonstration of all-optical, nanoscopic spatial control of molecular reaction yields on isolated silica nanoparticles. By tailoring nearfields with waveform-controlled linear and bicircular two-color laser pulses, and employing reaction nanoscopy, we probe the birth location of molecular fragments on the nanoparticle surface with an angular resolution around 8°. This corresponds to a spatial resolution of about 20 nm for 300 nm silica nanoparticles. Notably, a site-selective proton emission from the dissociative ionization of adsorbate molecules is observed, dependent on the polarization and relative phase of the two-color pulses. The findings are corroborated by classical trajectory Monte Carlo simulations based on strong field ionization in near-fields and quasi-static charge interactions.

The second part of the thesis advances on the previous work toward the spatiotemporal tracing of the reaction products with unprecedented spatial and temporal resolution at the nanometer-femtosecond scale. It demonstrates the first realization of pump-probe reaction nanoscopy to probe surface charge dynamics in individual silica nanoparticles. The study investigates the process of surface charge relaxation and its impact on the bond-weakening of the adsorbed molecular groups on single, isolated silica nanoparticles. The study offers a four-dimensional visualization of the surface charge density. It allows the distinction of the contributions of the underlying physical process comprising of diffusion and charge loss on different timescales, supported by semi-classical simulations. The simulations shed light

on the role of laser-induced surface charges in the weakening of the terminal O-H bonds at the interface, whose dynamics are caused by the redistribution of initially localized charge carriers.

The final part of the thesis presents a study focusing on the formation of trihydrogen cation on the surface of strong-field irradiated citrate-capped gold nanoparticles. The study elucidates how variations in shape can alter the reaction landscape of the nanoparticle surface by comparing the reaction products emitted from strong-field ionized spherical and faceted gold nanoparticles. The study underscores the significant role of charge localization in driving reaction dynamics, with steric effects contributing to the overall reactivity enhancement. It is shown that by leveraging the proton-rich environment created by laserinduced nanoparticle surface ionization, faceted gold nanoparticles demonstrate increased catalytic activity, highlighting their potential for various chemical transformations.

Overall, this thesis explores ultrafast nanoscale surface dynamics comprising an alloptical spatial control over nanoscopic reaction yields, revealing four-dimensional surface charge dynamics on nanoparticles, the impact of surface charges in bond-weakening and uncovering morphology-dependent effects on catalytic behavior modulation in gold nanoparticles. The ability to control and analyze surface reactions on nanoparticles paves the way for advancements in photocatalysis, atmospheric chemistry, and other fields reliant on these fundamental processes.

# Chapter 1 Introduction

The investigation of nanoscale phenomena has been a cornerstone in various scientific disciplines, providing profound insights into the fundamental processes governing matter at small scales [1]. At the nanoscale, the interactions between materials and their surrounding environment are predominantly dictated by surface properties, leading to unique phenomena and reactivity that differ significantly from bulk behavior [2]. The high surface-to-volume ratio and quantum confinement effects lead to distinctive electronic, optical, magnetic, and catalytic behaviors [3], making them indispensable in various scientific and technological domains [4]. Due to their unique properties, the interaction of nanoparticles with lasers has garnered substantial interest owing to the tunability, precision, and versatility offered by laser-based techniques [5]. The interaction of nanoparticles with laser fields induces intriguing phenomena such as plasmon resonances [6, 7], photothermal effects [8], nonlinear optical responses [9], and ultrafast dynamics [10, 11, 12, 13, 14], providing a fertile ground for exploring novel functionalities and applications.

An interesting phenomenon that arises from this synergy between nanoparticles and lasers is the utilization of laser-induced near fields to manipulate chemical reactions at the nanoscale [15, 16]. Near fields refer to the electromagnetic fields localized close to the surface of nanostructures, characterized by strong spatial confinement and enhanced field intensity compared to the incident light [17]. This phenomenon finds applications in sensing [18], surface-enhanced spectroscopy [19], and photothermal therapies [20]. Moreover, near fields can induce strong coupling between molecular excitations and plasmon resonances [21], giving rise to phenomena such as surface-enhanced Raman scattering [22] and surface-enhanced fluorescence [23]. In catalytic applications, near fields can facilitate the excitation of adsorbates to higher electronic states, lowering the activation energy barriers and promoting specific chemical reactions [24, 25]. In the presence of near fields, the absorption cross-section of molecules can be significantly enhanced due to the increased electromagnetic field intensity [26]. The precise control over near fields allows for selective excitation of desired reaction pathways, enabling unprecedented control over surface reactivity [27].

The interaction between molecules and nanoparticle surfaces, influenced by enhanced electromagnetic fields, results in a range of photophysical and photochemical effects [28].

This interaction is pivotal in various applications such as catalysis [29], sensing [18], and drug delivery [30]. For example, molecules may undergo enhanced absorption, emission, or scattering due to the proximity of plasmonically active nanostructures [31]. The binding of molecules to the surface of nanoparticles can occur through various intermolecular forces, such as Van der Waals interactions, hydrogen bonding, and chemical bonding [32, 33]. The adsorption behavior of molecules is influenced by factors such as surface chemistry, nanoparticle morphology, and environmental conditions [34, 35]. Nanoparticles provide a high surface-to-volume ratio, offering ample sites for molecular adsorption and catalytic reactions. The adsorption of molecules onto nanoparticle surfaces can lead to changes in their electronic structure, chemical reactivity, and optical properties [36, 37]. Understanding and controlling the surface chemistry of the adsorbed molecules under light irradiation is essential for optimizing the performance of nanomaterials in diverse applications [36].

Enhanced near-field chemistry, hot carrier transfer to surface molecules, and heat generation via electron-phonon coupling are key factors driving the surface reactivity of nanoparticles [15, 16]. While these processes can unfold on varying length scales and timescales, they take place simultaneously. This intricacy introduces difficulty in isolating their distinct impacts on resulting chemistry. Characterization techniques such as X-ray photoelectron spectroscopy, scanning electron microscopy, and transmission electron microscopy provide valuable insights into the surface chemistry and morphology of nanoparticles [38]. Despite significant progress in understanding molecular adsorbate reactions on nanoparticle surfaces, several challenges remain in controlling and optimizing these processes. One major challenge is the limited understanding of the dynamics and kinetics of surface reactions at the nanoscale. Traditional experimental techniques often lack the spatial [39, 40] and temporal [41, 42] resolution required to probe individual reaction events occurring on nanoparticle surfaces.

The generation and manipulation of near fields rely on the careful design of nanostructures and the precise control of laser parameters [43]. Various techniques have been developed to tailor the properties of near fields, including the choice of nanoparticle material, size, shape, and surface morphology [44]. For instance, noble metal nanoparticles such as gold and silver are commonly employed due to their strong plasmonic resonances in the visible and near-infrared regions of the electromagnetic spectrum. While advanced nanofabrication methods like electron beam lithography and focused ion beam milling offer precise control over the physical structure of nanomaterials [45], they can be limited in their ability to dynamically tune the near field. In contrast, adjusting the incident angle, polarization, and wavelength of the laser light provides a dynamic and tunable approach for manipulating near fields [46, 47].

One such means to leverage the unique properties of nanostructures to generate and manipulate local near-fields with unprecedented precision is provided by strong-field laser fields [46, 47]. Achieved by focusing few-cycle ultrashort laser pulses to a small focal volume, these strong laser fields can exceed intensities of  $10^{14}$  W/cm<sup>2</sup>, sufficient to manipulate atomic potentials [48, 49]. Ultrashort laser pulses within strong field regimes offer two significant advantages. Firstly, their very short duration enables the precise observation and analysis of phenomena occurring on ultrafast timescales. Secondly, by concentrating en-

ergy within a short timeframe, these pulses achieve significant intensity levels, facilitating the exploration of nonlinear light-matter interactions. In the past decade, the field of strong-field physics has undergone a significant transformation, extending its traditional focus from atoms and molecules to encompass nanostructures, surfaces, and solids [50]. This expansion has been fueled by the prospect of harnessing ultrafast light-wave-driven processes for applications such as nanoelectronics and catalysis [51].

Under strong field irradiation, molecules on nanoparticle surfaces are subjected to intense laser fields, leading to a variety of photoinduced processes such as ionization, fragmentation, and desorption [52, 46]. The presence of localized electromagnetic fields near the nanoparticle surface can further modify the interaction between molecules and intense laser fields, leading to enhanced ionization efficiency and modified reaction pathways [53, 54]. This occurs through emission of highly energetic electrons after the interaction between strong-field lasers and nanoparticles, inducing a highly positively charged state around the nanoparticle surface [51]. The strong positive potential generated at the surface can also confine few electrons, preventing their escape [55]. The interaction between adsorbate molecules and the nanoscale environment, comprising of the localized charge interactions between the trapped electrons and generated positive surface charges can lead to the emergence of novel reaction pathways.

Photoelectron spectroscopy constitutes one of the key methodology studying strong field laser-nanoparticle interactions. Studies on nanospheres and nanotips exposed to strong laser fields revealed fundamental light-matter interaction processes, consistent with theoretical models predicting the behavior of plasmonic fields near these nanostructures [56, 57, 50]. The technique works by analyzing photoelectrons emitted during the lasernanoparticle interaction, and is particularly advantageous due to the sensitivity of photoelectrons to sub-wavelength spatial features and ultrafast temporal changes. Localized electromagnetic fields near the nanoparticle surface can significantly impact electron acceleration [12]. Electrons can interact with the nanoparticle surface, leading to rescattering events that influence their final energy and momentum. Localized charges within the nanoparticle can interact with the photoelectrons, affecting their trajectories. The analysis of the energy and angular distribution of emitted electrons helps in understanding the fundamental factors contributing to the acceleration of these electrons, including near-field enhancement, surface rescattering, and various charge interactions [58, 51, 59, 60, 61].

Despite significant progress in understanding strong-field induced photoelectron emission on nanoparticles, a critical challenge lies in unraveling the underlying nanoscale surface chemistry. One approach to address this challenge involves studying the emission of charged fragments from the dissociation of adsorbate molecules on nanoparticle surfaces. When intense laser fields interact with the nanoparticle surface, these adsorbate molecules fragment and emit charged fragments. This process, driven by enhanced near-fields and surface properties, can act as a sensitive probe for local reaction yields and dynamics [52]. Analyzing the emitted fragments sheds light on the role of near-fields and charge interactions in shaping molecular behavior on these surfaces. Studying the dissociative ionization fragments of molecular surface adsorbates could provide a means of probing surface reaction pathways and identifying reaction intermediates with high sensitivity and specificity.

Reaction nanoscopy [52], builds upon the principles of reaction microscopy [62] to investigate strong-field ionization phenomena with nanosized targets. It enables the measurement of the three-dimensional momentum distribution of ions generated by a strong laser pulse from the surface of an isolated nanosystem injected into ultra-high vacuum. By integrating mass spectrometry and momentum imaging, reaction nanoscopy provides a robust approach to understanding nanoparticle surface dynamics under laser irradiation. It was first introduced by Rupp et al. [52] in 2019 and opened doors to studying spatially resolved ultrafast reaction dynamics on nanoparticles. The pioneer work demonstrated its application in studying selective proton generation during laser-induced dissociative ionization, highlighting its potential for advancing nanoparticle photochemistry. The study investigated spatially selective proton generation in laser-induced dissociative ionization of ethanol and water on nanoparticles. Interestingly, the observed anisotropic proton momentum distribution correlated with the near-field amplitude on the nanoparticle surface, effectively mapping the spatial variability of the reaction yield. Furthermore, semi-classical simulations successfully reproduced the experimental observations, revealing directional emission hot spots and change in their spatial distribution with increasing nanoparticle diameter.

Since its inception, reaction nanoscopy has witnessed continuous exploration and refinement. Rosenberger et al. [63] showcased its utility in differentiating reaction yields from single nanoparticles and their clusters. This work highlighted the dominance of cluster signals over single nanoparticle signals at low intensities. Another study employed reaction nanoscopy to investigate the formation of trigydrogen cations via bimolecular reactions involving water molecules on the surface of laser-irradiated silica nanoparticles [53]. This research underscored the role of aerosolized silica nanoparticles in intense femtosecond laser fields acting as catalysts in forming these exotic molecular entities through non-traditional pathways. Further exploration extended the applicability of reaction nanoscopy to different polarizations and wavelengths [46]. The study concluded that near-field imaging can be extended to mid-infrared wavelengths and arbitrary ellipticities of laser polarization. Additionally, it validated a semi-classical model based on static-field charge generation, providing a qualitative description of the experimental observations. This work also shed light on the surface composition of nanoparticles and clarified the role of alcoholic solvents in the observed ion spectra. The study revealed that the ions generated from the nanoparticles primarily originate from covalent bonds with the silica surface rather than from physisorbed solvent molecules. Reaction nanoscopy's versatility extends beyond single nanoparticles. Another recent study demonstrated the application of reaction nanoscopy to strong-field ionized nanodroplets of propanediol (PDO) [64]. The technique's sensitivity to the near-field around the droplet allowed for the in-situ characterization of the average droplet size and charge. Furthermore, by comparing the behavior of different PDO isomers (1,2-PDO and 1,3-PDO), the study revealed intriguing variations in ion emission and fragmentation channels. The specific alignment of 1,2-PDO molecules on the surface led to an enhanced production of methyl cations. This observation highlights reaction nanoscopy's potential for investigating the influence of molecular orientation on surface chemistry at the nanoscale.

This thesis builds upon these advancements in reaction nanoscopy. The layout of this thesis is structured as follows. Chapter 2 explores the theoretical underpinnings of the interaction between strong-field lasers and nanoparticles. It delves into the models utilized to comprehend the phenomenon of strong-field ionization of nanoparticles, as well as the mechanisms governing surface charge generation and ion emission during this interaction. This theoretical framework establishes the foundation for interpreting and contextualizing the experimental findings presented later in the thesis. Chapter 3 elucidates the experimental procedures implemented in this thesis. This chapter provides a comprehensive overview of the methodology employed for three-dimensional momentum imaging of the charged fragments from molecular dissociation. It outlines the techniques utilized for nanoparticle synthesis, the optimization of laser parameters, and the operational intricacies of the reaction nanoscope itself. The chapter elaborates on the procedure for measuring the time-of-flight (TOF) and impact positions of ions using a delay-line detector, along with the utilization of a channeltron electron multiplier to discern ions from nanoparticles and background gas.

Chapter 4 presents the experimental demonstration of all-optical nanoscopic spatial control over the reaction yield landscape on the surface of individual nanoparticles. This achievement opens avenues for reliable manipulation of photocatalytic chemical reactions on nanoscale surfaces. The chapter elaborates on the utilization of waveform-controlled laser pulses to achieve precise control. It also discusses the achieved spatial resolution by analyzing phase-dependent variations in fragment emission angles. The validation of results through semi-classical simulations establishes a consistent mapping between the initial birth position of dissociated protons from the adsorbate molecules and their final momentum, promising versatile applications across various nanosystems.

Expanding the capabilities of reaction nanoscopy, Chapter 5 focuses on tracking nanoscale surface charge dynamics. It presents a novel four-dimensional visualization of non-linear charge dynamics on single  $SiO_2$  nanoparticles irradiated by strong laser fields, offering real-time insights into surface charge redistribution processes. Semi-classical simulations further elucidate the roles of diffusion and charge loss in shaping these dynamics, providing valuable understanding of their impacts on catalytic reactions and chemical bonding.

Chapter 6 broadens the application of reaction nanoscopy to metallic gold nanoparticles, probing into trihydrogen cation formation and exploring the influence of nanoparticle morphology on ionization yields. Through a comparative analysis between citrate-capped spherical gold nanoparticles and polyhedral counterparts, the chapter reveals intriguing disparities in behavior. It underscores the significance of morphology and size-dependent effects in catalysis, emphasizing the heightened reactivity observed in faceted gold nanoparticles due to increased surface inhomogeneties and charge localization. These findings shed light on the complex interplay of factors such as charge localization, steric effects, and environmental conditions in modulating reactivity and catalytic behavior, showcasing the potential of faceted gold nanoparticles in diverse chemical transformations.

In conclusion, understanding ultrafast nanoscale surface dynamics in nanomaterials is important for both research and practical applications. This thesis highlights the significance of studying how nanoparticles behave when exposed to intense laser pulses, which can help improve nanotechnology in areas like catalysis. This thesis provides insights into the intricate processes governing strong-field laser-nanoparticle interactions, whose understanding could be leveraged to potentially design and engineer nanomaterials with tailored functionalities. By explaining the concepts and techniques used, this thesis contributes to our understanding of nanomaterials and paves the way for future advancements in nanoscience. The following chapters will discuss the experimental results, offering insights into these light-nanoparticle interactions and their potential applications.

### List of publications by the author with relevance to this thesis

- R. Dagar, P. Rosenberger, W. Zhang, M. Neuhaus, B. Bergues, C. Costa-Vera, and M. F. Kling. "Trihydrogen cation formation on strong field-ionized gold nanoparticles", *In preparation* (2024)
- R. Dagar<sup>†</sup>, W. Zhang<sup>†</sup>, P. Rosenberger, T. M. Linker, A. Sousa-Castillo, M. Neuhaus, S. Mitra, S. Biswas, A. Feinberg, A. M. Summers, A. Nakano, P. Vashishta, F. Shimojo, J. Wu, C. Costa-Vera, S. A. Maier, E. Cortés, B. Bergues, and M. F. Kling. "Tracking Surface Charge Dynamics on Single Nanoparticles", *In press, Science Ad*vances (2024)

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### Chapter 2

### **Theoretical Background**

When transitioning from bulk materials to nanoparticles, several notable differences emerge [2]. Nanoparticles bridge the gap between individual atoms/molecules and macroscopic materials, necessitating specialized theoretical models to capture their unique properties. Unlike bulk materials, nanoparticles exhibit size-dependent properties. Their increased surface area to volume ratio alters their electronic structure, increases the importance of surface effects, and steers the collective behavior of atoms towards more localized interactions [7]. These changes significantly impact the ionization dynamics when nanoparticles interact with strong laser fields generated by few-cycle intense femtosecond pulses. As a result, standard models of atomic and bulk ionization become inadequate, highlighting the need for tailored approaches to accurately characterize nanoparticle ionization phenomena. One such computational framework is provided by the  $M^{3}C$  model [65]. The name stands for Mean field, Mie theory, and Monte-Carlo. The M<sup>3</sup>C model has been successful in explaining various laser-nanoparticle interaction experiments, particularly for spherical dielectric nanoparticles. It initially focused on describing photoemission dynamics of electrons [58, 55, 51, 12] and also adapted for ion emission in the first reaction nanoscopy results [52]. However, later it was realized that the precise details of electron dynamics within the nanoparticle are not essential for capturing the key features observed in strong-field ion emission experiments and a more computationally efficient approach was developed by Rosenberger et al. [63]. This chapter delves into a semi-classical modeling based on the static-field model developed by Philipp Rosenberger [66] for elucidating strong-field laser-nanoparticle interaction and subsequent ion emission. The static-field model, which is simply referred as Classical Trajectory Monte-Carlo (CTMC) simulations, has been adapted to work in this thesis. We will further extend the model to explore the effects of varying nanoparticle shapes on the resulting proton momentum distributions from faceted gold nanoparticles.

### 2.1 General description

#### 2.1.1 Nanoparticle field enhancement

Electromagnetic waves interact with nanoparticles in fascinating ways, with the effect mainly depending on the material of the nanoparticle and the wavelength of the light. When light interacts with a metallic nanoparticle, its free electrons collectively oscillate at a specific frequency, resonating with the incoming light wave. This creates an intense, localized electric field around the nanoparticle, significantly amplifying the original electromagnetic field strength [17]. This enhances light absorption and scattering which can be maximized at any specific wavelength by tuning the size and shape of the nanoparticles [8, 7]. The material properties of the nanoparticle also influence field enhancement. Different metals exhibit varying plasmonic responses, affecting the intensity and nature of the localized field. In contrast to metals, dielectrics lack free electrons for localized surface plasmon resonances [67]. However, they can exhibit field enhancement through mechanisms such as Mie scattering and photonic resonances [68]. Mie scattering arises from the interaction between incident light and the electric dipole moment induced within dielectric nanoparticles, leading to scattering and absorption of light resulting in localized electric fields within the particle. Photonic resonances occur when the size of the dielectric nanoparticle matches specific fractions of the wavelength of incident light, resulting in constructive interference and field enhancement within the nanoparticle. Composition and material properties play a pivotal role in shaping the behavior of dielectric nanoparticles when exposed to external electromagnetic fields [68]. Maxwell's equations in conjunction with boundary conditions and material properties, such as the refractive index, govern the propagation and confinement of electromagnetic fields within nanoparticles [69, 70].

One theoretical framework used to understand the interaction of electromagnetic waves with nanoparticles is the Mie theory [71]. Developed by Gustav Mie in 1908, Mie theory is an exact solution to Maxwell's equations for the scattering and absorption of electromagnetic waves by a homogeneous, spherical particle. It provides a framework to calculate various properties like scattering cross-section, extinction cross-section, and absorption efficiency based on the particle size, material properties (including complex refractive index for metals), and the incident light wavelength. Mie theory serves as the primary framework for understanding how light interacts with spherical dielectric nanoparticles. This is because dielectric nanoparticles can be more readily produced in homogeneous and spherical shapes compared to metallic ones. For dielectrics, Mie theory predicts the scattering and absorption efficiency at different wavelengths. It also identifies peaks in these spectra corresponding to Mie resonances, which are crucial for understanding the optical behavior of the nanoparticles. While Mie theory can predict resonance behavior (including peak positions and intensities) for metallic nanoparticles as well, it doesn't explicitly account for surface plasmon resonance at the atomic level. However, for larger metallic nanoparticles (compared to the electron mean free path), Mie theory predictions can still accurately capture the overall resonance behavior. It's important to note that the simple implementation of Mie theory assumes homogeneity throughout the particle, which might not hold true for all nanoparticles, especially those with complex structures. Moreover, Mie theory is best suited for the scenario involving spherical particles. For non-spherical shapes, alternative methods are necessary. Therefore, alternative methods like Finite-Difference Time-Domain (FDTD) simulations are extensively utilized for modeling light interaction with nanoparticles [72]. FDTD solves Maxwell's equations numerically on a discretized grid, allowing for the accurate simulation of electromagnetic wave propagation and scattering in complex nanostructures, considering their geometry, material properties, and incident field characteristics. Also, commercial FDTD solvers are easily available due to their widespread availability. This thesis employs the Ansys Lumerical FDTD (release 2022 R1, version 8.27.2898) simulation package to model the near-field interactions between light and nanoparticles.

#### Finite-Difference Time-Domain (FDTD) Simulations

FDTD offers a powerful numerical approach by discretizing both space and time within Maxwell's equations. This discretization creates a three-dimensional grid where each point represents a specific location and time, holding the values of electric and magnetic fields. The core strength of FDTD lies in its ability to solve Maxwell's equations iteratively at each grid point. This iterative process involves solving finite difference approximations of the original differential equations, effectively calculating how the electromagnetic fields evolve over time. By considering the discrete interactions between neighboring grid points, FDTD builds a comprehensive picture of the electromagnetic field's behavior within the simulated space. Unlike analytical methods limited to specific geometries, FDTD readily handles diverse nanoparticle shapes, sizes, and material compositions. It facilitates the study of field localization, enhancement, and the electromagnetic response of nanoparticles across various conditions [73].

Our simulations employed Lumerical's FDTD solver to calculate the distribution of enhanced electric fields around various nanoparticles. The method involved several key steps. The first step involved defining the simulation region and incorporating the target nanoparticle's geometry. Lumerical's library offers a convenient selection of shapes, including a sphere used in our case for simulating dielectric silica nanospheres. For more complex geometries, like the faceted gold nanoparticles discussed in Chapter 6, CAD files can be imported. The material properties of the nanoparticle (silica or gold in this case) were assigned from Lumerical's extensive material database. The nanoparticle was then precisely positioned within the simulation region. The simulation domain and time window were carefully chosen. The time window needs to be long enough to reach a steady state and the simulation domain must be large enough relative to the nanoparticle and light source to avoid unwanted interactions or reflections from the boundaries affecting the results. A computational mesh was then generated throughout the domain, balancing the need for sufficient resolution to capture near-field details with computational efficiency. A crucial aspect is setting up the initial electromagnetic field. We employed the "totalfield scattered-field (TFSF)" source throughout our simulations. The laser characteristics, such as pulse duration, wavelength, and polarization, significantly influence how the light

interacts with the nanoparticle. As described in various chapters, different incident field configurations were used depending on the specific study. These parameters can significantly affect the near-field enhancement and, consequently, the ionization rates within the nanoparticle. The electromagnetic field distributions across the entire simulation region were monitored using a 3D "frequency domain field and power monitor" tool within the software.

Selecting the appropriate monitor type (time-domain or frequency-domain) in Lumerical FDTD simulations is crucial for accurate data interpretation. Time-domain monitors record the electric field as a function of time at each grid point in the simulation space. The electric field in the time domain monitor output is presented solely as real numbers, reflecting the instantaneous strength of the field at each time step. However, the frequency domain monitors transform the time-domain electric field data into the frequency domain using Fourier transforms providing insights into the spectral components of the electric field. The resulting data is complex, consisting of both magnitude and phase information of the field. The key distinction lies in interpreting the absolute value when considering the absolute value of a complex number versus the absolute value of its real part. The absolute value of the real number directly reflects the actual magnitude of the electric field at a given time point. Taking the absolute value of the complex field output, however, can be misleading as complex numbers in electromagnetism represent a combination of amplitude and phase. In our case, time-domain monitors were the preferred choice, especially when analyzing the time evolution of the electric field and its intensity.

Finally, the field enhancement factor  $(\alpha)$  was calculated. This factor quantifies the amplification of the electromagnetic field near the nanoparticle at each point (grid point, **r**) within the simulation volume. It is obtained by comparing the maximum electric field intensity around the nanoparticle to the incident field intensity. Mathematically, the value of  $\alpha$  is represented as follows:

$$\alpha(\mathbf{r}) = \frac{\max_t |\mathbf{E}_{\text{FDTD}}(\mathbf{r}, t)|}{\max_t |\mathbf{E}_{\text{in}}(t)|}.$$
(2.1)

The FDTD simulations, due to their fine grid spacing and numerous time steps, produced a significant amount of data. To improve computational efficiency, we employed the following approximation which involved scaling the incident electric field  $(E_{in}(t))$  at each grid point (r) by the corresponding field enhancement factor  $(\alpha(\mathbf{r}))$ . This approach provides a faster way to estimate the actual electric field  $(E(\mathbf{r}, t))$  within the simulation, without significantly affecting the ion emission results for the systems under study. The approximation is mathematically represented by the following equation:

$$\mathbf{E}(\mathbf{r},t) = \mathbf{E}_{FDTD}(\mathbf{r},t) \approx \alpha(\mathbf{r})\mathbf{E}_{in}(t).$$
(2.2)

Here,  $\mathbf{E}_{FDTD}$  represents the electric field obtained directly from the FDTD simulation. The key advantage of this approach lies in its ability to leverage the pre-calculated enhancement factor ( $\alpha(\mathbf{r})$ ) to efficiently estimate the actual electric field for varying experimental intensities throughout the simulation without the need of running the FDTD solver multiple times. Also, in FDTD simulations involving multiple light sources to generate the required electric field waveform, such as the two-color linear and bicircular fields used in Chapter 4, careful normalization of the overall incident electric field is essential. Normalization ensures a fair comparison of the resulting field enhancement factor ( $\alpha$ ) by taking into account the strengths of each individual source. The particular approach taken here involved calculating the total incident intensity by summing the intensities of each component field. This ensures that the resulting  $\alpha$  reflects the enhancement relative to the combined initial light field from all the components used, rather than being simply scaled by the number of source components used to simulate different electric field configurations. This is essential for interpreting the results of simulations involving complex light field configurations.

### 2.1.2 Strong-field photoionization

Few-cycle femtosecond laser pulses can be extremely intense, which can be focused to peak intensities reaching into the range of  $10^{12}$  to  $10^{16}$  W/cm<sup>2</sup> offering a unique regime for exploring light-matter interactions in solids [74, 48, 56, 49, 75]. These pulses can induce strong-field ionization, a phenomenon where the intense electric field of the laser pulse overcomes the binding potential of electrons in the solid, leading to their ejection [49]. Strong-field ionization disrupts the equilibrium distribution of electrons via distorting their electric binding potential within the solid. In contrast to the classical picture of electrons bound to atomic nuclei, the electronic structure of solids is described by energy bands [56]. As a result, when solids are exposed to the intense femtosecond laser pulses some of the bound electrons gain enough energy to escape from their bound states and become essentially free electrons.

The Keldysh parameter  $(\gamma)$  is a dimensionless quantity that characterizes the dominant ionization regimes in strong-field ionization [76] based on the interplay between the laser field strength  $(E_0)$ , angular laser frequency  $(\omega)$ , and the material's ionization potential  $(I_p)$ as following

$$\gamma = \sqrt{\frac{I_p}{2U_p}},\tag{2.3}$$

where,  $U_p$  is the pondermotive potential defined as

$$U_p[\text{eV}] = \frac{e^2 E_0^2}{4m_e \omega^2} = 9.33 \times \lambda[\text{m}]^2 \times I[10^{14} \text{W/cm}^2].$$
(2.4)

Here e is the electron charge,  $m_e$  is the electron mass,  $\lambda$  denotes the central laser wavelength, and I is the laser intensity, given by  $I = \frac{1}{2}\epsilon_0 c E_0^2$ , where  $\epsilon_0$  represents the vacuum permittivity and c is the speed of light. Based on the Keldysh parameter, the two primary regimes that govern the process of strong-field ionization are: multiphoton ionization and tunneling ionization. In the tunneling regime ( $\gamma \ll 1$ ), the strong electric field dominates the ionization process, while multiphoton ionization becomes more prominent for larger  $\gamma$  values. In multiphoton ionization, an electron absorbs multiple photons (n) from the laser pulse in a sequential manner, acquiring sufficient total energy  $(nh\omega)$  to overcome the material's ionization potential  $(I_p)$  and escape the solid [77, 78]. In tunneling ionization, electrons tunnel directly through the potential barrier without absorbing multiple photons. When the electric field strength surpasses a critical threshold, it can distort the potential barrier experienced by the electrons at the solid's surface. This allows for a finite probability of electrons tunneling through the classically forbidden region and escaping the solid [79, 80].

Following ionization, the freed electrons are subject to the intense laser field, experiencing significant acceleration and acquiring kinetic energy leading to the generation of highly energetic photoelectrons [49]. In the context of nanoparticles, strong-field ionization exhibits additional complexities due to size-dependent effects (surface-to-volume ratio, field propagation effects, etc.) leading to a more prominent role of surface states and potential barrier modifications at the surface [25]. Electrons localized near the surface are more likely to experience a weaker effective potential barrier, enhancing the probability of tunneling ionization compared to the bulk material [56, 12, 51]. The extent of this effect depends not only on the laser parameters (intensity, pulse duration, and wavelength) but also on the intrinsic properties of the nanoparticle material, including its work function and surface morphology [61, 81].

Throughout this thesis, the experimental conditions typically fall within the tunneling regime, characterized by  $\gamma < 1$ . In this context, we describe photoionization rates using the Ammosov-Delone-Krainov (ADK) ionization rate [79] for dielectric nanoparticles, and the Fowler-Nordheim tunneling rate [82] for metallic nanoparticles, unless otherwise specified. This choice of models serves to effectively capture the photoionization dynamics under the experimental conditions of interest.

### 2.2 Semiclassical modeling

Inspired by the static-field model described in detail in [66], our semi-classical approach to modeling strong-field ion emission dynamics can be broken down into the following steps: A few-cycle, linearly polarized laser pulse interacts with a sub-wavelength nanoparticle, inducing a localized enhancement of the laser's electric field near the nanoparticle's surface. This strong electric field triggers two key processes: ionization of the nanoparticle surface via electron tunneling, where surface electrons escape the nanoparticle due to the intense field generating positive surface charges, and some multiphoton ionization of the adsorbed surface molecules leading to the dissociation of protons. The positions of these positive charges and the ejected protons are statistically determined using Monte-Carlo rejection sampling method based on the distribution of the local near-fields. Following this, the classical Newton's equations of motion are used to simulate the propagation of the protons. Their movement is primarily influenced by the electrostatic field generated by the newly formed positive surface charges on the nanoparticle. As a result, this framework allows us to simulate the final momentum distribution of the emitted protons. Figure 2.1 provides a visual summary of the basic model, with further details discussed in the following sections.

### 2.2.1 Surface ionization and charge sampling

Following the generation of near-field distributions around the nanoparticle's surface using FDTD simulations, the subsequent step involved calculating the probability distribution of nanoparticle surface ionization corresponding to the near-field distribution. We employed a two-state model to capture the essential features of the electron ionization via population transfer between bound and free states on the nanoparticle surface (described in detail in [66]). The bound state represents an electron localized within the nanoparticle's potential well due to the electrostatic attraction of atomic cores. The initial state population is denoted by  $P_{b}(t)$ . The free state signifies an electron liberated from the nanoparticle due to the interaction with the laser field. The population of electrons in this state is denoted by  $P_f(t)$ . The interaction between the intense laser field, characterized by its time-dependent electric field strength (E(t)), and the nanoparticle drives a population transfer from the bound state  $(P_b)$  to the free state  $(P_f)$ . This process is quantified by the time-varying tunneling ionization rate  $(\eta(E(t)))$ . The rate is calculated utilizing the ADK formula [79] with reference to an ionization potential of 10.2 eV for silica and the local electric field described in Eq. 2.2. For the case of gold nanoparticles, the Fowler-Nordheim tunneling ionization rate is used instead ADK rate but the rest of the process remains the same.



Figure 2.1: Schematic of the basic CTMC simulations outlining the steps towards determining the proton momentum distribution during the strong-field ionization of a silica nanoparticle.

The dynamics of the electron population in these states can be described by a set of coupled ordinary differential equations:

$$\frac{dP_b}{dt} = -\eta(E(t))P_b. \tag{2.5}$$

This equation expresses the rate of change  $(dP_b/dt)$  of the bound state population  $(P_b)$ . The negative sign indicates a decrease in the bound state population as electrons transition to the free state. The rate of decrease is directly proportional to the instantaneous ADK rate  $(\eta(E(t)))$  at a specific time (t) and the current bound state population  $(P_b)$ .

$$\frac{dP_f}{dt} = -\frac{dP_b}{dt} = +\eta(E(t))P_b.$$
(2.6)

This equation highlights the population transfer and conservation of total electron population. The rate of increase in the free state population  $(dP_f/dt)$  mirrors the decrease in the bound state population. While the ADK rate  $(\eta(E(t)))$  describes the instantaneous probability of an electron transitioning, the actual probability of finding an electron in the free state at a specific time (t) is represented by the ionization probability  $(P_{ion}(t))$ . This probability reflects the cumulative number of electrons that have transitioned to the free state relative to the total number undergoing ionization. It provides a quantitative measure of the laser pulse's effectiveness in removing electrons from the nanoparticle over a particular time period. The ionization probability can be calculated by integrating the rate equation for the free state population  $(dP_f/dt)$  over the laser pulse duration. Prior to the interaction with the laser pulse, the system is assumed to be entirely in the bound state. This translates to initial conditions for the integration process, expressed as  $P_b(t = -\infty) = 1$  and  $P_f(t = -\infty) = 0$ . The solution for the population of the free state,  $P_f(t)$ , is then given by:

$$P_{ion} = P_f(t = \infty) = 1 - \exp\left(-\int_{-\infty}^t \eta(E(t'))dt'\right).$$
 (2.7)

The limit  $(t \to \infty)$  is replaced by a final time  $t_f$  for practical computational purposes. This final time is chosen sufficiently large such that the free state population,  $P_f(t_f)$ , closely approximates the true steady-state ionization probability,  $P_f(t = \infty)$ . The model predicts that very high electric fields lead to saturation of the ionization probability  $(P_f(t = \infty))$ at nearly 1. This signifies that under such intense fields, electrons in the bound state have an extremely high probability of escaping, essentially all of them will transition to the free state. At moderate electric field strengths, the probability of ionization increases linearly with the strength of the field. In simpler terms, a stronger electric field directly translates to a higher probability of electrons escaping the nanoparticle. This linear relationship implies a predictable rise in ionization as the field strength grows. At low electric field strengths, the chance of an electron escaping becomes less dependent on the instantaneous field strength itself. Instead, the total accumulation of the ionization rate over time becomes the dominant factor signifying a gradual ionization process. Also, due to spatial variations in the electric field and consequently, the ionization probability across the nanoparticle surface, directly calculating it for every point on-thefly would be inefficient. Eq. 2.2 offers an alternative by approximating polarization and field evolution as spatially constant. This allowed us to calculate the ionization probability for just two extremes (lowest and highest field strengths) and a few intermediate points within the simulation volume. By using a sufficient number of intermediate points, we used interpolation to obtain ionization probabilities for all other field enhancement values. This approach significantly improved the computational efficiency.

#### Surface Charge Sampling

After establishing the overall ionization probability for different electric field strengths across the nanoparticle surface, the subsequent step involved determining the spatial distribution of actual ionization events. To achieve this, we employed the Monte-Carlo rejection sampling method [83]. Initially, we calculated the probability of ionization at each point on the nanoparticle surface based on the local electric field strength, thereby creating a "probability map" indicating the likelihood of an electron escaping from a specific location. Subsequently, the rejection sampling method was utilized to randomly select points on the surface according to the calculated ionization probability distribution, drawn from a uniform distribution.

To generate uniformly sampled points on the surface of a sphere, 3D points were randomly generated within a unit cube first, and then each point was projected onto the surface of a sphere by dividing its coordinates by its Euclidean distance from the origin. These sampled points were later scaled by the desired sphere radius. However, for nanoparticles with intricate, faceted geometries, the aforementioned method for spherical surfaces was not directly applicable. This challenge was tackled by first acquiring a 3D CAD model of the specific shape of the nanoparticle, to generate a 3D mesh corresponding to it. The acquired mesh was then used to create a downsampled point cloud representation. This collection of points represented the surface of the acquired nanoparticle geometry. Finally, the spatial coordinates of these points within the point cloud were extracted.

All the uniformly sampled points were assigned with a random value between 0 and 1. The algorithm then randomly selects points on the nanoparticle surface from the uniformly sampled points. The value of each randomly chosen point is compared to the corresponding ionization probability value at that location on the map. If the value of the randomly chosen point falls below the ionization probability, the point is "accepted" as a valid ionization event. Conversely, if the random value is higher, the point is rejected, and a new random point is chosen. By repeating this sampling process a large number of times, we could statistically reconstruct the spatial distribution of ionization events across the entire nanoparticle surface. This Monte-Carlo approach allows us to efficiently account for the spatial variations in the electric field and the resulting non-uniform ionization probability across the nanoparticle. Additionally, care is taken to obtain a continuously varying distribution of charges across space from the discrete distribution of electric field values provided by the FDTD simulations. This is because discrete charges, limited to grid points provided

by the FDTD grid, could create artifacts or necessitate excessively fine grids. To overcome this limitation, the electric field obtained from the FDTD simulations (Eq. 2.2) is linearly interpolated. This interpolation allowed us to calculate the ionization probability for any point in space, enabling a continuous distribution of charges for more accurate simulations.

While the rejection sampling method doesn't explicitly limit the number of samples drawn, the number of accepted candidate positions directly translates to the number of positive charges placed on the nanoparticle surface. This, in turn, significantly influences the subsequent charge dynamics simulation. The generated positive surface charges represent the overall ionization of the nanosurface, which signifies the removal of electrons. Ideally, the total number of removed electrons could be determined by multiplying the ionization probability per atom with the number density of the nanoparticle material. The above calculation would give us the charge density across the entire surface layer which then can be integrated over space to obtain the total charge on the nanoparticle surface. However, in reality, not all electrons possess enough energy to escape the nanoparticle [55]. To maintain computational efficiency, this effect was neglected. Consequently, the total positive surface charge is approximated as an effective quantity, capturing the net effect of electron removal without explicitly simulating the energy distribution of individual electrons. This effective quantity is approximated through an experimental fit parameter which is determined based on the measured kinetic energy of protons ejected from the nanoparticle surface during the ionization process. The obtained number represents the total effective positive charge on the surface. The model's good quantitative agreement with experiments (see later chapters) confirms the effectiveness of using an effective surface charge to account for electron-ion interactions on the dynamics of the dissociated protons.

A key advantage of this model is that it avoids the need for separate calculations for different orientations of faceted nanoparticles relative to the laser polarization. This is particularly important because the alignment of a faceted nanoparticle's surface features with the laser focus significantly impacts the degree of field enhancement experienced. For example, a nanoparticle aligned along its vertices will exhibit different field enhancement compared to one aligned along its faces. To account for this variation in field enhancement and the resulting impact on ionization probabilities across different orientations, we utilized Monte-Carlo integration to calculate the ratios of accepted samples for different orientations. These ratios can then be scaled by the total surface charge obtained from any initial fit of any chosen orientation. While the initial fit for the total surface charge can be obtained from any chosen orientation, to ensure consistency across different nanoparticle shapes, we scale the ratios from Monte-Carlo integration by the total surface charge obtained from the orientation that exhibited the highest field enhancement factor in the FDTD simulations.

### 2.2.2 Ion generation and propagation

Alongside modeling point like static surface charges, our simulation encompasses evaluating the dissociative ionization yield originating from chemisorbed and physiosorbed molecules on the surface. Predominantly, we focus on tracking the trajectories of protons, which emerge as the most common dissociating fragments from both, silica and gold nanoparticles in our case. The surface composition of the nanoparticles to highlight the origin of protons is discussed in detail in Chapter 3. To capture the spatial variability of the dissociative ionization probability of protons across the surface of a nanoparticle, we followed a similar approach to previous studies [63, 46, 64], which is also described in detail in [66]. The model assumes that surface molecules undergo dissociation via a multiphoton dissociative ionization process.

The multiphoton dissociation yield in the context of laser-induced ionization depends significantly on the intensity of the laser field. As disscussed earlier, multiphoton processes involve the simultaneous absorption of multiple photons (n) by the molecule, where the combined energy  $(n\hbar\omega, \text{ with } \hbar\omega$  representing the energy per photon) must overcome the ionization potential  $(I_p)$  of the involved molecules for electron emission. These absorbed photons provide the necessary energy for ionization and dissociation. To account for the multiphoton nature of the interaction, our model describes the dissociative ionization yield of proton emission through the following relationship, which exhibits a nonlinear dependence on the intensity of light:

$$Y \propto I^n = I^{I_p/\hbar\omega},\tag{2.8}$$

where, n is estimated as  $n = I_p/\hbar\omega$ . Here, Y denotes the ion yield, and  $I = I(\mathbf{r})$  represents the local intensity of the laser pulse, which varies across the nanoparticle surface due to variations in the near-field enhancement factor from point-to-point. Consequently, the ion yield also exhibits spatial variations, with regions experiencing higher intensity having a proportionally greater number of ejected protons. Also, the number of photons required for ionization (n) is not just dependent on the material's ionization potential but also on the energy carried by each photon  $(\hbar\omega)$ , which in turn is determined by the laser's wavelength. This concept becomes particularly important in two-color experiments discussed later in this thesis where two different laser wavelengths (the fundamental and the second-harmonic) are used. In such scenarios, the minimum number of photons required for ionization is typically calculated based on the lower wavelength (higher energy photon) because it provides the most efficient pathway for overcoming the ionization potential. The approach captures how variations in both laser intensity and photon energy influence the likelihood of ionization across the nanoparticle surface.

Leveraging the rejection sampling technique previously described for selecting surface charge locations, we adopted a similar strategy to sample the birth positions of ejected protons across the nanoparticle surface. The sampling highly depended on the distribution of ionization probabilities calculated using the power-law in Eq.2.8 and hence the intensity of the laser (I). Furthermore, in reality, the density of adsorbed molecules on the nanoparticle surface may vary spatially. To model this spatial variability of the adsorbed surface molecules, we multiplied the ion yield, Y, with a Gaussian function along the radial coordinate (r), introducing a spatial dependence to the ion yield representing as Y(r). This Gaussian function reduces the ion generation in close proximity to the nanoparticle surface. The process can be expressed mathematically as following:

$$Y(r) \propto I^n(r) \cdot \exp\left(-\frac{(r-R)^2}{2\sigma_r^2}\right).$$
 (2.9)

Here,  $\sigma_r$  represents the standard deviation of the Gaussian distribution, and R denotes the radius of the nanoparticle for spherical particles. For non-spherical nanoparticles, such as those with facets, a slightly modified approach is implemented. In this case, the surface is represented by a collection of uniformly sampled random points. For each randomly chosen point (i) on the surface, the value of R is substituted with the Euclidean distance  $(R_i)$ of the selected point from the origin to determine the Gaussian distribution required for sampling around that point. This substitution ensures effective Gaussian filtering around all faces and edges on the surface, accounting for their varying distances from the origin. Overall, the process leads to a more accurate representation of the spatial distribution of ion yields and thus, proton birth positions.

Once generated, the protons are then propagated under the influence of the static electric field created by the surface charges. The electric field acting on a mobile ion at any given position  $(\mathbf{r})$  within the system is approximated by summing the contributions from all the static point charges present on the nanoparticle surface as described in the following equation:

$$\mathbf{E} = \frac{e}{4\pi\epsilon_0} \sum_{i=1}^{N_s} \frac{\mathbf{r} - \mathbf{r}_i}{\|\mathbf{r} - \mathbf{r}_i\|^3}.$$
(2.10)

Here, e is the elementary charge,  $\epsilon_0$  represents the free space permittivity,  $N_s$  denotes the total number of surface charges and  $\mathbf{r}_i$  is the position vector of the *i*-th surface point charge. The propagation of the dissociated ions, which in our case is mostly protons, is then simulated by numerically integrating Newton's equations of motion. The simulation continues until the momentum of each mobile ion reaches a state where it no longer experiences significant changes between consecutive time steps. We also acknowledge the infinite range of the Coulomb potential, implying that the ion's potential energy may not be entirely converted into kinetic energy even at the termination of the simulation. To address this, we employed a momentum rescaling technique. The final momentum vector of each ion is adjusted to ensure it aligns with the calculated total energy. This rescaling step assumes that by the conclusion time of the simulations, the ions have moved far enough away from the nanoparticle surface that only the magnitude (length) of their momentum vector might slightly change, while the overall direction remains relatively fixed.

For computational efficiency, our model neglects the electrostatic Coulomb interactions between the ejected electrons and protons. While these interactions do exist, we posit that their influence on the behavior of the protons is minimal compared to the dominant effect of the charged nanoparticle surface. We believe the primary factor governing the final momentum of the ejected protons is their interaction with the charged surface they originated from. Additionally, we consider the influence of electrons on the direction of proton emission to be negligible. This simplification allows us to focus our computational resources on analyzing the dominant interaction responsible for shaping the final momentum distribution of the ejected protons.

#### 2.2.3 Charge diffusion and loss

Our discussion thus far has only focused on the interaction timescale of the laser and the nanoparticle surface. This interaction involved the generation of surface charges on the nanoparticle surface with the removal of electrons and the dissociation of adsorbed surface molecules via multiphoton dissociative ionization. While the initial near-field induced ionization of the nanoparticle surface is localized on the surface, the nature of the surface charges is dynamical. Understanding how these surface charges redistribute over time is crucial for comprehending how nanoparticles ultimately influence and participate in various surface reactions. To model this post-laser charge relaxation-phase, we extended the CTMC simulations to incorporate surface charge redistribution through diffusion. These extended simulations are denoted as d-CTMC, with "d" signifying the diffusion component. We model this by implementing a diffusive random walk process for the initially sampled localized surface charges, simulating their movement across the nanoparticle surface. The model further incorporates a charge loss mechanism to account for an additional decrease in surface charge density as elucidated in Chapter 5. The surface charge diffusion and loss mechanisms have emerged as the predominant processes governing charge relaxation process post the initial laser interaction. The qualitative agreement observed between simulation results and experimental data, as presented in Chapter 5, is providing support to our understanding.

The diffusion of surface charges on the surface of a spherical nanoparticle can be effectively modeled using a 3D random walk. This simulation approach is similar to the Brownian motion of particles, where their movement is characterized by random displacements in three-dimensional space [84]. The mean square displacement, denoted as  $\langle x^2 \rangle$ , quantifies the average distance a charge travels from its starting position after a given time interval (t). This is mathematically given as:

$$\langle x^2 \rangle = 6Dt, \tag{2.11}$$

where, D is the diffusion coefficient. It quantifies the rate of diffusion. For a single time step, represented by  $\tau$ , the mean square displacement simplifies as:

$$\langle x^2 \rangle = 6D\tau. \tag{2.12}$$

This time step defines the temporal resolution of the simulation. Smaller time steps allow for a more accurate representation of the diffusion process, but require more computational resources. Therefore, it was crucial to maintain a balance between accuracy and computational efficiency. This balance was achieved by checking the convergence of the results for different values of the time step. Solving Eq. 2.12 for the root mean square, we obtain the average distance traveled by a charge within one time step, expressed as following:

$$\Delta = \sqrt{\langle x^2 \rangle} = \sqrt{6D\tau}.$$
(2.13)
To model the inherent randomness of charge movements during diffusion, the simulation employs a Gaussian distribution for step sizes in a random walk. This choice offers advantages in terms of both numerical efficiency and its ability to realistically capture the stochastic nature of the process. The number of simulation steps required for the diffusion process is determined by dividing the total time window by the chosen time step size. During each step, individual protons are propagated away from the surface according to Newton's laws, considering the influence of the electrostatic field generated by the surface charges. This iterative process ultimately yields the final 3D distribution of momentum for the simulated protons, capturing their behavior over the entire desired time frame.

During the simulations, it's crucial to restrict the random walk of charges to the nanoparticle's surface. This ensures the charges remain physically on the surface, preventing them from "jumping" outside the nanoparticle or getting lost within the bulk of the material. As each point on the spherical nanoparticle surface can be expressed in terms of the elevation and azimuth angle  $(\theta, \phi)$ , the model utilizes the tangential unit vectors  $(\hat{\mathbf{e}}_{\theta}$  and  $\hat{\mathbf{e}}_{\phi})$  to calculate the mean square displacement at each time step. These coordinates ensures the random walk remains confined to the curved spherical surface. Additionally, if a proposed step would move a charge beyond the sphere's boundary, the model adjusts the step size to project it in back onto the surface if necessary.

The model utilizes the following exponential charge decay equation [85] to describe the phenomena of charge loss:

$$Q(t) = Q_0 e^{-kt} + Q_{\text{residual}}.$$
(2.14)

Here, Q(t) represents the remaining surface charges at any time t,  $Q_0$  represents the initial number of surface charges present at the beginning of the simulation, k is the charge decay constant which characterizes the rate of charge loss over time, and  $Q_{\text{residual}}$  is the residual charge remaining after the simulation's time window. The value and distribution of  $Q_0$ , the localized surface charge upon near-field induced ionization depends on the experimental conditions, such as the size and material of the nanoparticle, laser parameters such as wavelength, intensity as described in the section on surface charge generation. The value of the charge decay constant is determined as a fit parameter to the experimental data, similar to the diffusion coefficient. The  $Q_{\text{residual}}$  factor accounts for the possibility that not all charges decay within the simulated time window.

# Chapter 3

# **Experimental Techniques**

# 3.1 Nanoparticle samples

### 3.1.1 Silica nanoparticles preparation and characterization

The  $SiO_2$  samples used in the thesis were mostly synthesized through collaborative efforts of Dr. Ana Sousa-Castillo in the group of Prof. Emiliano Cortés and Prof. Stefan A. Maier at LMU Munich.

Highly monodispersed silica nanoparticles were prepared using the classic Stöber method [86] with some modifications to achieve the desired size. Typically, particle formation is initiated through the hydrolysis and condensation of alkoxysilane precursors, often tetraethylorthosilicate (TEOS), in a solution containing alcohol, water, and ammonia as a catalyst, as illustrated in Fig. 3.1. Specifically, TEOS is hydrolyzed in a mixed ethanol/ammonia solution, leading to the formation of silanol monomers, where the ethoxy groups (-Si-OEt) are replaced with silanol groups (-Si-OH). Subsequently, the silanol monomers undergo condensation between two silanol groups, resulting in the formation of branched siloxane clusters. These clusters are further involved in the nucleation and growth of silica particles.

**Reagents and Materials.** Tetraethoxysilane (TEOS,  $\leq 98\%$ ), ethanol (EtOH, absolute), and ammonia solution (NH4OH, 27 wt. % in water) were purchased from Sigma-Aldrich. A Millipore Milli-Q was used to a final resistivity of  $18.2 \text{ M}\Omega \cdot \text{cm}$  and a total organic content of  $\leq 3 \text{ ppb}$  using a Mit Q-POD<sup>®</sup> Nanopure system.

Synthesis of Silica Nanoparticles. Briefly, 1.7 ml of TEOS solution was added to a solution containing ethanol (18.12 ml), ammonium hydroxide (1.96 ml), and water (3.21 ml). This mixture was stirred at room temperature for 2 hours. The excess reagents were removed by three centrifugation-redispersion cycles with ethanol (6000 rpm, 10 min).



Figure 3.1: Schematic illustration of the mechanism of the formation of silica nanoparticles by sol-gel process [87, 88].

#### Characterization

Size and Morphology. The size and morphology of the silica nanoparticles were characterized using Transmission Electron Microscopy (TEM, JEOL1020) operating at 80 kV and Scanning Electron Microscopy (SEM, ZEISS ULTRA PLUS). In general, SEM images display surface topography and provide 3D information, while TEM images reveal internal structures at higher resolutions, offering insights into composition and nanoscale details. As an example, the morphological analysis of the silica nanospheres carried out for a particular batch using transmission electron microscopy (TEM) is shown in Fig. 3.2A, and using scanning electron microscopy in Fig. 3.2B. The uniform distribution of SiO<sub>2</sub> nanoparticles with a diameter of  $(288 \pm 12)$  nm is confirmed by these images as shown in Fig. 3.3A.

 $\zeta$  potential. The zeta potential measurement of silica nanospheres (-30 mV) was carried out at 25°C by Dynamic Light Scattering (DLS; Zetasizer Nano ZSP, Malvern Instruments Ltd., Malvern, U.K). For example, the hydrodynamic diameter (HD) of the TEM and SEM



Figure 3.2: (A) TEM micrographs of  $SiO_2$  nanoparticles (B) Corresponding SEM images.

images displayed in Fig. 3.2 was measured as  $(300 \pm 10)$  nm using the DLS technique. Furthermore, the zeta potential for the 300 nm SiO<sub>2</sub> nanospheres was determined to be  $\sim$ -42 mV, as depicted separately in Fig. 3.3B. The zeta potential is a representative of their surface charge, indicating their stability in a solution. It reflects the electrostatic repulsion between particles and predicts their tendency to aggregate or disperse.

The concentration of the SiO<sub>2</sub> nanoparticle solution typically ranged from 0.1 g/l to 1 g/l in this thesis. Prior to each experiment, the particle suspension underwent sonication for approximately a minute to get rid of heavy clusters. Notably, lower concentrations yielded a cleaner stream of nanoparticles predominantly composed of single particles, while higher concentrations led to an increased occurrence of agglomerates. Hence, a trade-off was maintained to balance the frequency of ionization events and the presence of clusters. The Reaction Nanoscope facilitated testing these conditions, where the emission of protons exhibited a distinct dipolar pattern with single nanoparticles, while the presence of clusters caused a broader emission pattern that tilted towards the laser's polarization direction [63].



Figure 3.3: (A) Size distribution obtained from the TEM images,  $D = (288 \pm 12) \text{ nm}$ . (B) Measured zeta potential using DLS technique,  $\zeta$  potential = -42 mV.

#### 3.1.2 Gold nanoparticles preparation and characterization

The gold nanoparticles used in this thesis were bought commercially from Sigma-Aldrich and Nanocomposix. The gold nanoparticles bought from Sigma-Aldrich (742031, 742007) were purchased with an optical density of 1 with stabilized suspension in citrate buffer with a high monodispersivity. From Nanocomposix, NanoXact gold nanospheres - bare citrate, were bought with different sizes (AUCN10, AUCN50, AUCN100). They were provided at a concentration of 0.05 mg/ml in 2 mM sodium citrate solution. The sodium citrate solution is essential to prevent the nanoparticles from agglomeration. The NanoXact gold particles exhibit a distinct color in solution, appearing either as a ruby red hue or a yellow-red shade, contingent upon their respective sizes. Because of their small dimensions, minimal mass, and remarkably high ratios of surface area to volume, once nanoparticles form bonds or aggregate, separating them becomes impossible.

The nanoparticle solutions were used with the same concentration as bought in the experiments because it was realized that dilution even with water resulted in the formation of clusters. This can be due to several reasons. Initially, the presence of citrate ions in the original solution serves to stabilize the nanoparticles by forming a protective layer around them, hindering their aggregation. However, when water is introduced to dilute the solution, the ionic strength decreases, changing the  $\zeta$  potential and disrupting this stabilizing effect. Consequently, the diminished concentration of stabilizing agents reduces the repulsive forces between nanoparticles. The electrostatic repulsion that previously kept the particles dispersed diminishes, allowing them to come into closer proximity, thereby facilitating their tendency to aggregate. Additionally, altering the solvent conditions by adding water may lead to changes in the interaction between the nanoparticles and the surrounding environment. This change can affect the nanoparticles' solvation layer, reducing the protective influence provided by the citrate ions and promoting particle-particle interactions, ultimately fostering agglomeration or the formation of larger clusters. In contrast, SiO<sub>2</sub> nanoparticles were found much more stable even upon dilution in water and ethanol primarily due to their inherent surface properties, uniform size and shape. Additionally, their surface charges, stemming from silanol groups, generate electrostatic repulsion between particles, preventing their aggregation even upon dilution.

## 3.2 Nanoparticle delivery system

A dedicated nanoparticle delivery system facilitates the generation and injection of a highly focused stream of individual nanoparticles into an ultra-high vacuum environment (with a pressure around 2 x  $10^{-10}$  mbar) inside the reaction nanoscope. This system employs a multi-stage process to attain the desired characteristics of the nanoparticle stream. Initially, a commercial atomizer (model 3076, TSI) aerosolizes the nanoparticle suspension. The nanoparticle suspension is continuously fed into the atomizer through a metal capillary immersed in the nanoparticle suspension encounters a high-velocity gas jet generated by pressurized gas passing through a narrow orifice. Argon is typically used as the carrier gas for all experiments mentioned in the thesis, at a pressure of  $\sim 1.4$  bar at the inlet. The interaction between the high-pressure gas and the liquid suspension results in the generation of an aerosol – a collection of micron-sized droplets – with each droplet containing a few nanoparticles. In principle, the gas pressure and nozzle size can be adjusted to alter the droplet size and distribution, while the density of nanoparticles within the aerosol stream is dictated by the initial concentration of the nanoparticle suspension. The atomizer operates in recirculation mode, where a portion of the generated aerosol is continuously returned to the atomizer for re-entrainment in the gas jet. This practice minimizes sample wastage and promotes a more uniform droplet size distribution.

The aerosol stream is then passed through a counter-flow membrane dryer (Perma Pure, PPMD-700-48S) to ensure the removal of any residual solvent from the wet aerosol. It is composed of a Nafion membrane connecting two concentric tubes. The process involves directing the moist aerosol through the Nafion membrane, which selectively permits the passage of water or alcohol vapor without affecting the individual nanoparticle or the carrier gas. Simultaneously, we used dry compressed air to flow in the opposing direction, facilitating the removal of moisture due to the humidity gradient established within the tube through the counter-flow system. Subsequently, the impactor, is placed at a sharp 90° bend along the flow path. It consisted of a slender opening measuring 0.71 mm, and a stainless steel plate situated 2 mm away from the aperture. Any nanoparticle clusters or large particles carried in the flow are blocked after hitting this plate, only allowing individual nanoparticles or very small clusters in the flow path. Subsequently, the nanoparticle stream traverses a T-piece situated atop a high-efficiency particulate air (HEPA) filter. One outlet of the T-piece connects directly to the inlet of the reaction nanoscope. The other outlet vents to ambient air via the HEPA filter, facilitating the reduction of the aerosol source pressure to 1 atm. This pressure is necessary for the downstream aerodynamic lens to function effectively during nanoparticle injection into the vacuum [89]. The HEPA filter functions as a safety measure, capturing any nanoparticles that might escape from the aerosol stream into the lab air.

The aerodynamic lens used in this work is based on the design mentioned in the PhD thesis of H. Bresch[89]. It works by channeling an aerosol stream through a converging nozzle, designed to regulate the gas flow. We used a glass nozzle with a diameter of  $\sim 190 \,\mu\text{m}$ , which suited best for our configuration, and optimally tested for  $300 \,\text{nm}$  SiO<sub>2</sub> nanoparticles. Following the glass nozzle, the nanoparticle containing gas flow is directed through a series of tubes with different lengths and aperture sizes collectively acting as focusing lenses. These lenses serve to converge and then diverge the gas flow, which plays a crucial role in the nanoparticle focusing process, influencing particles of varying sizes differently. Smaller particles, which are more susceptible to the heightened airspeed, tend to follow the streamlined flow more effectively. The nanoparticle stream transitions from the aerodynamic lens into a two-stage differential pumping system equipped with 1 mm diameter conical skimmers, producing a focused particle beam of approximately 500  $\mu$ m in diameter.

# 3.3 Laser setup

For all the experiments described in this thesis, a home-built optical parametric chirpedpulse amplification (OPCPA) system centered around at the wavelength of 2  $\mu$ m with a repetition rate of 100kHz is used. The OPCPA used is based on the Innoslab technique seeded by a fiber laser system [90].

The laser system consisted of a 100 MHz Ytterbium-based fiber oscillator. The laser pulses are stretched and pre-amplified in a fiber amplifier before further amplification using an InnoSlab amplifier, producing 1030 nm compressed pulses with a 110 W power output and 1 ps duration. This output is branched further into 3 different stages. One of them is used to generate a supercontinuum for expanding the laser spectrum, another one to generate the second harmonic, both of them are then collectively sent to a Nonlinear Optical Parametric Amplification (NOPA) stage. The NOPA output is then used as the pump for a Difference Frequency Generation (DFG) process combined with the third branch of the initial beam which creates the seed laser at 2 µm for the next Optical Parametric Amplification (OPA) stage. This stage is pumped by the 1030 nm beam, with an energy of 1 mJ, and is used to amplify the output of the 2 µm laser beam achieving a final output of 6W laser power. In general, we used 30 mm of sapphire at the output for further pulse compression resulting in laser pulses with a pulse duration of  $\sim 25$  fs. We added a long-pass spectral filter (Thorlabs FELH0600) to the beam path to block out any unwanted optical signals at lower wavelengths. Various optical configurations are tailored to suit the specific requirements of each experiment, as elaborated in the respective chapters.

# **3.4** Reaction nanoscope

The reaction nanoscope, also known as the nanoTRIMS, employs three-dimensional ion momentum spectroscopy, an upgraded form of Recoil Ion Momentum Spectroscopy [62] designed for targets at the **nano**scale. A complete schematic is shown in Fig. 3.4. The laser pulses are focused using a concave silver mirror with a focal length of 75 mm using a back-focusing geometry inside the reaction nanoscope reaching intensities on the order of  $\sim 2-5 \times 10^{13}$  W/cm<sup>2</sup>. This focused beam intersects with the nanoparticle jet within the interaction volume, where electrons and ions are generated due to the nanoparticle interaction with the strong laser fields.

The spectrometer has two detectors, one at each end. The ion side is equipped with a time- and position-sensitive detector consisting of a stack of microchannel plates (MCPs) and a delay-line detector (DLD) (DLD80, RoentDek Handles GmbH) allowing for the reconstruction of their full 3D momentum distributions using their impact positions and time-of-flight (TOF) as described in the following sections. On the other end of the spectrometer, a channeltron electron multiplier (MAGNUM 5901, Photonis, USA) is placed to record the electrons emitted with each laser shot. Inside the spectrometer, evenly spaced electrodes help create a homogenous electric field ranging from around  $\sim 100 \text{ V/cm}$  to 200 V/cm. The spectrometer further incorporates electroformed meshes (from Precision



Figure 3.4: Working and schematic of the reaction nanoscope - it consists of the nanoparticle injection source and the ion momentum spectrometer. The nanoparticle injection source starts with a *nanoparticle suspension*, which is then drawn into an *atomizer*. Here, pressurized gas breaks the suspension into tiny droplets/aerosol containing a few nanoparticles each. The *membrane dryer* removes excess solvent, and the *impactor* eliminates large clusters. The nanoparticle stream then travels through a T-piece, where one outlet connects to the inlet of the reaction nanoscope and the other vents into ambient air to reduce the pressure to 1 atm connected inline with a *HEPA filter*. The HEPA filter acts as a safety measure to capture nanoparticles that might escape the aerosol stream. An *aerodynamic lens* focuses the nanoparticle stream before it enters the main chamber of the reaction nanoscope, where it intersects with focused laser pulses. The reaction nanoscope features an ion momentum spectrometer, comprised of an array of evenly spaced electrode rings separated by 100 k $\Omega$  resistors (R). These rings maintain a consistent electric field when a high voltage is applied [91]. Upon ionization within the chamber, the electric field directs the resulting ions and electrons towards opposite sides of the spectrometer for detection. The ion detector utilizes a *microchannel plate* (MCP) to record the time-of-flight of the ions, while a *delay line detector* (DLD) determines their position. On the electron side, a *channeltron* functions as the electron detector. It provides a time-integrated signal, which directly reflects the total number of generated electrons.

Eforming, USA) positioned in front of the detectors to optimize its performance. These meshes counteract any fringing fields emanating from the electrodes, thereby ensuring a uniform electric field throughout the entire spectrometer volume. Also, to improve detection efficiency, the spectrometer utilizes an increased electric field gradient between the mesh and the MCP, which effectively accelerates ions for improved signal strength.

#### **3.4.1** Electron detection and nanoparticle events

The distinction between strong-field ionization events originating from nanoparticles and those stemming from background molecules, such as adsorbed solvent or carrier gas, is a critical aspect of the experiments related to reaction nanoscopy. This differentiation is important for gaining insights into the unique laser-nanoparticle interaction dynamics under varying conditions. The process of strong-field ionization of nanoparticles produces a large number of electrons compared to the ionization of individual atoms or small molecules.

Our experimental approach involved careful analysis and quantification of the electron signal in coincidence with ions, allowing us to disentangle the contributions from nanoparticles and background molecules. The electron detection is a critical component of the setup and as mentioned earlier, is carried out via a channeltron electron multiplier, which is responsible for quantifying the release of electrons. In experiments, the channeltron's sensitivity is intricately linked to its voltage settings. Typically, the top voltage of the channeltron is set around 1000 V, while the bottom voltage is set around 3600 V. Maintaining a voltage difference below 2600 V ensures optimal working conditions, striking a balance between maximizing gain and preventing undesired effects like electron backscattering. When switching on and off the channeltron, a systematic approach is followed to ensure safety and prevent voltage-related issues. While switching on, the top knob is turned to the required voltage settings first then followed by changing the voltage settings at the bottom side of the channeltron. Reversely, while turning the setup off, the bottom voltage knob is always brought to 0 first, followed by adjusting the top voltage knob. This sequential process is crucial to avoid exceeding the maximum specified voltage difference of 2600 V, ensuring the channeltron's stable and reliable operation in the experimental setup.

The channeltron signal was processed through capacitive decoupling from its anode, followed by subsequent sampling using a high-speed analog-to-digital converter (fADC4, RoentDek Handels GmbH) and subsequent time integration. This resulted in the generation of a negative electronic pulse for each detected electron or electron bunch by the channeltron. Three different quantification methods were employed: measuring the width, amplitude, and integral of the electronic pulse. The integral of the channeltron signal was identified as the preferred approach for the analysis of nanoparticle ionization events and the comparison of electron yields in coincidence with ions. This choice was motivated by two primary considerations. Firstly, the channeltron signal resulting from nanoparticle ionization could present multiple peaks within a single pulse, leading to varied width values at the defined threshold and compromising signal reliability. Secondly, in comparison to the amplitude of the electron signal measured around  $\sim 10 \,\mathrm{mV}$ , nanoparticle ionization could yield a substantial number of electrons simultaneously detected by the channeltron,

resulting in amplitudes reaching a few hundred mV, occasionally surpassing 500 mV.

To address the challenge posed by the fADC4's limited capacity to handle such large signals and the potential risk of damaging its channels, a spark protection plug was introduced before sending the channeltron signals directly to the fADC4. This precaution effectively eliminated high-amplitude channeltron signals, setting an upper threshold value on amplitudes during signal processing. While safeguarding the equipment, this measure also introduced a challenge—setting the upper threshold might lead to misinterpretations, as small ionization events could be mistakenly considered on par with those involving a significant number of electrons released from nanoparticle ionization. Therefore, considering the overall integral of the signal pulse ensured reliability and accuracy of the measurements, contributing to a better understanding of nanoparticle ionization dynamics in the experiments.

Detection of ions concurrently with a minimal or zero electron signal indicated the ionization of individual gas-phase molecules. Differentiating between electrons stemming from background ionization (involving solvent or carrier gas molecules) and those resulting from strong-field ionization of nanoparticles requires establishing a threshold value. To determine this threshold, experiments were conducted using only the carrier gas or pure solvent in the nanoparticle injection setup, excluding any dissolved nanoparticles. This comparison enabled the distinction between electrons originating from background ionization and those from strong-field ionization of nanoparticles. In Figure 3.5A, a typical ion spectrum along the laser's polarization direction versus TOF is presented, resulting from the ionization of a 300 nm SiO<sub>2</sub> nanoparticle using a 2  $\mu$ m laser at 100 kHz. The corresponding spectrum of the channeltron signal integral is illustrated in Fig. 3.5B.



Figure 3.5: (A) A typical position vs tof spectrum of positive ions produced by the strongfield ionization of a 300 nm SiO<sub>2</sub> nanoparticle using a 2 µm laser. The ions contributed by the background are enclosed by the red box, characterized by significantly lower kinetic energies. In contrast, ions resulting from nanoparticle ionization exhibit a distinct dipolar emission along the laser polarization direction and possess considerably higher energies. (B) The corresponding spectrum of the channeltron signal integral. The purple bar centered around zero represents background ionization events, while the orange curve signifies the electron signal derived from nanoparticle ionization events. In the inset (i), ions detected in coincidence with a low electron signal, corresponding to the purple peak, are illustrated. Inset (ii) provides a visualization of ions detected coincidentally with high electron signals, depicted by the orange curve as registered by the channeltron.

The images in the inset of Fig. 3.5B reveal the distinct separation of background events (inset (i)) from nanoparticle generated ionization events (inset (ii)), achieved through filtering based on the strength of the electron signal. The integral of the channeltron signals, particularly those associated with high electron count rates stemming from nanoparticle induced ionization events, was found to be substantially greater — orders of magnitude higher — when compared to signals from background gas. This significant disparity in the channeltron signal amplitude proved instrumental in differentiating molecular ionization and dissociation events occurring on the surface of nanoparticles. This aspect becomes even more crucial when distinguishing between events generated by nanoparticles under different conditions and correlating them with the electron signal to ascertain the specific regimes of ionization.

#### 3.4.2 Ion detection

After the ionization of the nanoparticles in the interaction volume, the resulting positive ions get accelerated in the homogenous field of the spectrometer towards the ion detector. The detector, as mentioned earlier is a combination of a chevron stack of MCPs for time detection and a delay-line anode for position detection.

The MCP functions as a particle amplifier, turning a single impinging positive ion into a cloud of electrons. Due to a high voltage difference between the MCP front and back, the impact starts a cascade of electrons, amplifying the original signal several orders of magnitude. The electrons exit the channels on the opposite side of the MCPs, where they are collected on the delay-line anode which is used for the two-dimensional position readout. It employed a pair of coiled wires comprised of a collection (signal) wire and a reference wire, rather than a single wire. This setup aims to diminish the noise caused by events like the simultaneous impact of two separate spots on a single wire. It measures the position of the centroid of the charge clouds that exit MCP by measuring the time it takes for electrical signals generated from their interaction to travel along the wires. This is accomplished by measuring the time difference between the arrival of the electronic signal at both ends of the delay line. The difference in arrival times at the adjacent ends of each delay-line is proportional to the position on the MCP in the respective dimension. The sum of these arrival times remains consistent within a few nanoseconds for each instance.

Both the MCP and the delay-line anode signals undergo amplification using an amplifier (Ortec FTA820A). Due to the variable height of the signals (voltage pulses), merely triggering the timing signal when reaching a specific threshold (a few mV) isn't adequate. Such an approach would lead to a time shift ("walk") contingent upon the pulse's height. However, they are passed through a constant fraction discriminator (CFD, Ortec 935) to increase the time resolution by activating the timing signal when a consistent portion of the pulse's height is attained. Typically, it divides the incoming signal into two parts, delays and inversely alters one segment, and subsequently reunites both segments. This process generates a bipolar pulse, and its zero-crossing point provides precise time data. This temporal data is then conveyed to the time-to-digital converter (TDC). This signal is directed to a time-to-digital converter (TDC8HP, Roentdek Handels GmbH) for extracting the timing information. The process of converting timing differences into positions, along with all other aspects of data acquisition, was accomplished through the utilization of the CoboldPC software developed by Roentdek Handels GmbH.

#### Ion momentum calculation

The initial momenta of fragment ions in three dimensions are determined by analyzing both their TOF and their respective positions within the spectrometer. As ions with a mass (m) and charge (q) travel through the spectrometer's uniform electric field  $(\vec{E})$ , they experience an acceleration force  $(\vec{F})$  in the direction of the field (here, let's consider it as z-direction). This force can be expressed as  $\vec{F} = m\vec{a}$ . Due to the uniform electric field, there are no force components acting on the ion in the x and y directions. Consequently, the ion's motion in these directions is characterized by constant velocity.

To determine the initial momenta, Newton's equation of motion  $(\vec{r} = \vec{r_0} + \vec{u}t + \frac{1}{2}\vec{a}t^2)$  is solved for all three dimensions (x, y, and z). Given the absence of forces in x and y, the acceleration component in those directions becomes zero. Therefore, the equations for the ion's position in x and y become:

$$x(t) = x_0 + \frac{p_x}{m}t,$$
(3.1)

$$y(t) = y_0 + \frac{p_y}{m}t.$$
 (3.2)

Also, the force on a charged particle in a uniform electric field  $(\vec{E})$  is given by  $\vec{F} = q\vec{E}$ . Since the electric field is solely in the z-direction, this translates to an acceleration in the z-direction of  $a_z = qE/m$ . The equation for the z-direction, considering the ion's initial position, velocity, and the acceleration due to the electric field, becomes:

$$z(t) = z_0 + \frac{p_z}{m}t + \frac{1}{2}a_zt^2 = z_0 + \frac{p_y}{m}t + \frac{qE}{2m}t^2 = l,$$
(3.3)

where, l is the distance between the interaction region and the ion detector.

Assuming the point of intersection between the laser and nanoparticle beam to be the origin of our chosen coordinate system, the initial position of the particle can be given as,  $(x_0, y_0 \text{ and } z_0) = (0,0,0)$ . Using the above equations, the initial momenta  $p_i$  of an ion can be calculated using the TOF (t) and the ions's impact position at the detector (x(t), y(t)) as follows:

$$p_x = m\frac{x}{t},\tag{3.4}$$

$$p_y = m \frac{y}{t},\tag{3.5}$$

$$p_z = m\frac{l}{t} - \frac{qE}{2m}t.$$
(3.6)

In essence, the initial momenta  $(p_i)$  of fragment ions in all three dimensions can be reconstructed by analyzing their TOF (t), position upon reaching the detector (x(t), y(t)), and the the length of the spectrometer (l). The TOF (t), mass (m) and charge (q) of the ion, distance traveled (l), and the uniform electric field  $(\vec{E})$  all contribute to the ion's trajectory and momentum determination. The ratio m/q can be retrieved from the TOF spectrum, though a spectrum calibration is required first as discussed in the following section.

Calibration of the time-of-flight spectrum. The calibration of a TOF spectrum involves the process of accurately determining the relationship between the time taken for ions to travel from their point of generation to the detector and their corresponding m/q. This calibration is essential for accurately identifying and quantifying the ions present in the spectrum. To calibrate the TOF spectrum effectively, a mixture of methanol, ethanol, and acetone was utilized. These compounds were selected for calibration purposes due to their well-defined mass peaks, which facilitated precise peak identification and served as reference points to the respective TOFs based on their characteristic mass-to-charge ratios (m/q). The TOF spectrum is shown in Fig 3.6. Some peaks can be challenging to identify clearly because different ions have the same m/q. To correlate the electronic signal from the nanoTRIMS with the TOF, calibration of the TOF spectrum depicted in Fig 3.6A becomes necessary. This calibration compensates for the fact that the time measured by the nanoTRIMS encompasses not only the TOF of the ions but also incorporates an inherent electronic delay,  $t = t_{TOF} + t_{electronics}$ . Single ionization events of single molecules generate ions with very low energies, which manifest as sharp peaks in the TOF spectrum. In this scenario, the ion primarily gains its momentum from the recoil of the released electron, with almost negligible influence from the momenta of the absorbed photons, leading to  $p_z$ = 0. Rewriting Eq. 3.6 as a function of  $t(\sqrt{m/q})$ , we have:

$$t(\sqrt{m/q}) = \sqrt{\frac{2ml}{E}}\sqrt{\frac{m}{q}} + t_{electronics}$$
(3.7)

This correlation can be described by a straightforward function y(x) = ax + b, where y = t and  $x = \sqrt{m/q}$ , allowing for a linear fitting as shown in the inset of Fig. 3.6B.



Figure 3.6: (A) The time-of-flight (TOF) spectrum obtained from a mixture comprising methanol, ethanol, and acetone exhibits discernible peaks corresponding to the ions produced. (B) The corresponding transformation into a m/q spectrum utilizing the equation delineated in the inset. The inset illustrates a linear correlation between the square root of the mass-to-charge ratio ( $\sqrt{m/q}$ ) and the measured time-of-flights (TOFs). This graphical representation proves invaluable during experimental procedures for real-time identification of various ionization fragments.

Plotting the TOF peaks for  $p_z = 0$  for various ions with known m/q ratios fixes the proportionality constant and offset for the linear fit as shown in the equation depicted in the inset plot of Fig.3.6B. The constant electronic delay ( $t_{electronics}$ ) can be derived from the fitting parameter b (the y-intercept). To obtain the correct TOFs and consequently accurate masses, this delay needs to be deducted from all recorded times. Consequently, m/q values are assigned to all the peaks for the single charged ions shown in Fig 3.6B.

The TOF calibration process allows for the removal of the electric field's influence from momentum calculations, requiring solely the knowledge of the spectrometer's ion side length (l). When  $p_z = 0$  the following equations are obtained:

$$a = \frac{qE}{m} = \frac{2l}{\tau_{m/q}^2},\tag{3.8}$$

where  $\tau_{m/q}$  signifies the TOF specific to the fragment's m/q for  $p_z = 0$ . Upon inserting this expression into eq. 3.6, it leads to the resulting equation

$$p_z = \frac{ml}{t} \left(1 - \frac{t^2}{\tau_{m/q}^2}\right) \tag{3.9}$$

This method stands as a preferable alternative to the direct computation of  $p_z$ , eliminating potential errors from the electric field and allowing for a more precise measurement of the spectrometer's length. Therefore, Eq. 3.9 is consistently employed in this thesis for calculating the momentum component aligned with the TOF axis.

# 3.5 Experimental troubleshooting

The density of nanoparticles within the interaction region is influenced by various factors, including the density of nanoparticles in the sample suspension, the aerosol generation process avoiding clusters, the aerosol transport system (comprising liquid reflow, drying, and pressure equalization), impactors used to reduce cluster presence, limitations of the aerodynamic lens system (including aperture sizes and nanoparticle size dependent throughput), and the distance from the final aperture to the interaction region.

The delay-line detector in the reaction nanoscope is designed for limited ion detection, but molecular adsorbates on nanoparticle surfaces often lead to challenges by contributing multiple ions upon ionization. Estimations based on silanol group density on silica particles reveal that even a 300 nm particle could potentially release a significant number of protons upon ionization[66]. Maintaining ion counts within the detector's optimal range is complicated by the nonlinear relationship between ion generation probability and laser intensity. Low intensities lead to nanoparticle cluster contributions[63], causing detector saturation and difficulties in proton detection. Higher intensities result in substantial ion generation, leading to MCP signal amplification and detector dead-time effects. These challenges impact data interpretation, emphasizing the need for cautious interpretation and the potential exploration of a different detector system to address these saturation issues. Few things can be kept in mind while dealing with this issue. Firstly, monitoring strong signals from the MCP offers insights into the extent of saturation. Secondly, minimizing undetectable signals by reducing laser intensity helps to maintain a more manageable data acquisition process and prevents excessive saturation. Lastly, acknowledging the nonlinear relationship between ion generation rates and detector saturation is crucial, as it highlights the limitations in entirely eliminating saturation in certain strong-field reaction nanoscopy experiments.

On the hardware side, the use of a Timepix detector may mitigate the problems associated with detector saturation observed with the current delay-line detector. Its ability to handle higher ion counts without experiencing saturation effects might offer a viable resolution to the challenges encountered when the delay-line detector reaches its limit. The delay-line anode detector determines position by measuring the time difference between signals arriving at both ends of wire pairs in each direction. This time delay corresponds to the position along the wire pair and is proportional to the position on the detector. In contrast, the Timepix detector utilizes a pixelated sensor, employing a semiconductor chip with an array of pixels that directly detect ion hits. Each pixel provides individual position information, enabling direct two-dimensional (x - y) localization of ion impacts. Unlike the delay-line anode detector, which determines position indirectly through time measurements, the Timepix detector offers direct positional information via its pixel array, allowing for simultaneous measurement of multiple ions' positions in a single shot.

# Chapter 4

# Controlling surface yields with tailored waveforms

The ability to precisely modify laser pulse waveforms presents a remarkable opportunity to create highly targeted optical near-fields surrounding nanostructures. This capability enables the manipulation of ultrafast processes at the nanoscale, both spatially and temporally. Several techniques, such as carrier-envelope-phase stabilized few-cycle pulses [12, 59] and phase-controlled linear two-color femtosecond pulses [92], have demonstrated the potential of this capability for electron emission. In this chapter, we demonstrate an all-optical control of ion emission, specifically protons, from the surface of isolated silica nanoparticles by using linear and circular two-color laser fields. By manipulating the relative phase between two-color components in femtosecond laser pulses, we demonstrate the ability to regulate the optical near fields around the nanoparticles, thus facilitating the spatiotemporal control over the reaction yields stemming from the interaction at the nanoscale. The findings elucidated in this chapter have been published in [93].

# 4.1 Introduction

In the field of strong field ionization, two-color laser pulses play a critical role. These pulses allow us to manipulate the relative phase ( $\phi$ ) between the two colors, typically a fundamental frequency ( $\omega$ ) and its second harmonic ( $2\omega$ ) within their combined laser waveform. This phase manipulation significantly impacts the ionization process, affecting the directionality, energy, and timing of emitted electrons and ions [94]. The waveform of such a two-color linear laser pulse can be represented as the sum of the two linear pulses at their different frequencies, the fundamental frequency  $\omega$  and its second harmonic  $2\omega$ :

$$E(t) = E_1(t)\cos(\omega t) + E_2(t)\cos(2\omega t + \phi), \qquad (4.1)$$

where  $E_1(t)$  represents the electric field envelope of the first pulse,  $E_2(t)$  represents the electric field envelope of the second pulse,  $\omega$  is the fundamental frequency, and  $\phi$  denotes the phase difference between the two components of the given frequencies. Figure 4.1C, D



Figure 4.1: (A) Electric field of a 18 fs laser pulse with 2 µm wavelength (B) Electric field of a 25 fs laser pulse with 1 µm wavelength, the second-harmonic of the 2 µm pulse (C) Combined field at phase difference,  $\phi = 0$ :  $E(t) = E_1(t) \cos(\omega t) + E_2(t) \cos(2\omega t)$  (D) Combined field with phase difference,  $\phi = \pi$ :  $E(t) = E_1(t) \cos(\omega t) - E_2(t) \cos(2\omega t)$ .

illustrates the electric field described by Eq. 4.1 for two different values of the relative phase difference,  $\phi$ . Figure 4.1A and Fig 4.1B illustrate the variation in the electric field waveform of the fundamental and second harmonic pulses, respectively, having different pulse durations. Fig 4.1C depicts the resultant electric field obtained by summing the individual fields of the fundamental and second harmonic frequencies, with a phase difference of zero ( $\phi = 0$ ). The combined waveform of the two-color pulses demonstrates the superposition of the two electric fields at their respective frequencies. Fig. 4.1D presents the combined field with a phase difference of  $\pi$ , emphasizing how the resulting waveform changes when the phase between the pulses is altered. This visualization is crucial for understanding the constructive and destructive interference patterns that arise from the summation of multiple electric fields. It highlights how different pulse configurations and phase differences impact the resulting combined electric field, thereby influencing the overall pulse characteristics which can manifest in their interaction with matter.

While linear polarization restricts the oscillation of the electric field of the laser pulses to a single axis, circular polarization involves the electric field vectors rotating in a circular manner as the wave propagates. This rotating motion provides additional degrees of freedom in controlling the characteristics of light pulses. The mathematical expression for a two-color bicircular laser field can be constructed by summing up its two circularly polarized components, each corresponding to different frequencies as follows, for a laser



Figure 4.2: (A) Co-rotating two-color bicircular fields with  $\phi = 0$  (B) Counter-rotating two-color bicircular fields with  $\phi = 0$  (C) Co-rotating two-color bicircular fields with  $\phi = \pi$  (D) Counter-rotating two-color bicircular fields with  $\phi = \pi$ .

pulse propagating in the *x*-direction:

$$E_{bicirc}(t) = E_1(t) \left( \sin(\omega t) \hat{\mathbf{e}}_y + \cos(\omega t) \hat{\mathbf{e}}_z \right) + E_2(t) \left( \pm \sin(2\omega t + \phi) \hat{\mathbf{e}}_y + \cos(2\omega t + \phi) \hat{\mathbf{e}}_z \right).$$
(4.2)

The unit vectors  $\hat{\mathbf{e}}_y$ ,  $\hat{\mathbf{e}}_z$  represent the laboratory frame. The  $\pm$  sign in the equation accommodates bicircular pulses with either the same or opposite helicities, thereby distinguishing between co-rotating (+) and counter-rotating (-) fields. In scenarios involving co-rotating fields, the electric field of the second pulse aligns its rotational direction with that of the first pulse, resulting in synchronized motion within the yz-plane. Conversely, in the case of counter-rotating fields, the electric field of the second pulse rotates in the opposite direction to that of the first pulse, thereby inducing a counteracting rotational movement within the yz-plane. Figure 4.2 illustrates the co-rotating and counter-rotating bicircular fields with circularly polarized pulses of the fundamental at 18 fs, 2 µm and the second harmonic with a pulse duration of 25 fs at 1 µm wavelength with  $\phi = 0$  in Fig. 4.2A and Fig. 4.2B respectively. Fig. 4.2C and Fig. 4.2D represent the combined circular fields with  $\phi = \pi$ .

Understanding the interplay between the relative phase of the two frequencies,  $\omega$  and  $2\omega$ , is crucial for elucidating the interaction between lasers and nanoparticles, enabling precise control over near-field enhancement and subsequent ionization dynamics at the

nanosurface. By adjusting the relative phase  $\phi$  between the two-color components, tailored manipulation and optimization of the laser-nanoparticle interaction can be achieved, leading to the creation of distinct chemical and optical hotspots on the nanoparticle surface. This manipulation induces asymmetric ionization of the nanoparticle surface, influenced by the spatial distribution of the near-fields, resulting in alterations to the momentum distributions of the emitted ions. The asymmetry arises from the preferential ionization of surface molecules adhered to the nanoparticle surface, varying depending on the prevalence of the optical hotspots. Modulation in the behavior of emitted ions, as a function of the relative phase  $\phi$  between the two-color pulses, allows investigation of the phase control effect of nanoparticle ionization. Constructive interference between the fields at certain phase differences may enhance ionization probability in specific directions, leading to enhanced yields in those regions of the ionization spectrum, while destructive interference may diminish ionization probability, resulting in reduced yields in other momentum regions. This interference leads to variations in the angular distribution or momentum of the emitted ions, resulting in asymmetrical features in the ion momentum spectra. For circularly polarized laser pulses, this leads to helicity-dependent ionization yields and angular distributions, as observed in the difference between laser pulse waveforms in Fig. 4.2 compared to those in Fig. 4.1. To explore this concept further, we employed reaction nanoscopy to track proton emission resulting from the dissociative ionization of molecular adsorbates on the surface of  $SiO_2$  nanoparticles, as discussed in subsequent sections of this chapter.

# 4.2 Experimental setup

#### Phase-locked interferometer

The experimental setup as illustrated in Fig. 4.3, utilized a phase-locked Mach-Zehnder interferometer to generate phase-controlled two-color laser fields with both linear and circular polarization. The interference between the two light paths within this setup was controlled by adjusting and locking the phase relationship between them to a reference phase as explained in the following.

Laser pulses from the custom-built optical parametric chirped pulse amplification system (OPCPA), centered at a wavelength of 2 µm and with a pulse duration of ~25 fs, as described in Chapter 3, served as the fundamental wave (FW). These pulses are directed into a 1.5 mm thick lithium niobate (LiNbO<sub>3</sub>) crystal, cut at a phase match angle of 45.6°, where a second pulse is generated at 1 µm, half the wavelength of the fundamental via sum frequency generation. Lithium niobate proves ideal for this experiment due to its broad transparency range in the mid-infrared, extending up to 3.5 µm, matching well with the 2 µm fundamental wavelength. Type I phase matching conditions cause the second harmonic components to be cross-polarized relative to the fundamental pulse. To enhance second harmonic (SH) generation efficiency, a telescope with a 2:1 ratio was positioned before the crystal. Two customized dichroic beamsplitters (Thorlabs BS2032)



Figure 4.3: Schematic of the phase-locked two-color interferometer. LiNb, lithium niobate; NDF, Neutral-density filter; BS, Dichroic Beam Splitter; HWP, half-wave plate; QWP, quarter-wave plate; WGP, wire-grid polarizer; CW, continuous-wave; CCD, Charged-coupled device; Ag (Silver) mirror.

were employed to separate and subsequently co-align the FW and SH pulses. Each arm of the interferometer contained additional optical components to adjust the light intensity and polarization independently. These components include half-wave plate, HWP (B.Halle Nachfl. GmbH,  $\lambda/2$  700-2500 nm), wire-grid polarizer, WGP (Thorlabs), and quarter-wave plate, QWP (B.Halle Nachfl. GmbH,  $\lambda/4$  700-2500 nm). The HWP was used to control the linear polarization of the FW and SH pulses as desired, the WGP was used to clean the polarization state of each pulse, and the QWP to control the ellipticity and helicity of the resulting pulses. The combination of the HWP with the WGP was utilized to control the intensities of the individual arms.

The circularly polarized laser pulses were created using the QWP by passing the linearly polarized pulses through the QWP at a 45° angle. A QWP is designed to introduce a phase difference of  $\pi/2$  (a quarter of a wavelength) between the orthogonal polarization components of incident light. When linearly polarized light passes through a QWP, it splits into two orthogonal polarization components, commonly known as the fast axis and the slow axis. The orientation of the QWP's fast axis relative to the incoming linearly polarized light is crucial for determining the helicity of the circularly polarized light. This importance arises from the birefringent nature of its material, which selectively alters the phase of light waves depending on their polarization. Considering the fast axis of the QWP as a reference point, aligning it at  $+45^{\circ}$  clockwise from the incoming light's polarization introduces a  $+90^{\circ}$  phase shift to the component parallel to the fast axis, while the slow axis component remains unchanged. This specific manipulation results in the generation of left-circularly polarized light, where the electric field vector rotates counterclockwise as it propagates. Conversely, aligning the fast axis at  $-45^{\circ}$  counterclockwise to the incoming light leads to a different outcome. While the fast axis component still undergoes a  $+90^{\circ}$  phase shift, the slow axis now experiences a  $-90^{\circ}$  shift. This combined effect produces right-circularly polarized light, with the electric field vector rotating clockwise as it propagates. When circularly polarized pulses of the same helicity emerge from different arms of the interferometer, they interfere constructively upon recombination, resulting in a semilunar pattern constructing co-propagating bicircular fields. This pattern occurs because the maxima and minima of the electric fields of the circularly polarized pulses align, reinforcing each other's intensity in certain regions while canceling out in others, leading to the formation of crescent-shaped intensity distributions as explained theoretically earlier. Conversely, when circularly polarized pulses of opposite helicities emerge from different arms of the interferometer, they interfere destructively upon recombination, resulting in a trefoil pattern. In this case, the interference between the left and right circularly polarized pulses leads to the formation of regions of high and low intensity arranged in a characteristic three-lobe shape. In summary, by adjusting the helicity of circularly polarized light in each arm of the Mach-Zehnder interferometer and controlling their relative phase difference, the phase-controlled, tailored laser waveform patterns were generated for the experiment.

Temporal synchronization between the two color pulses was achieved using a motorized delay stage (Smaract SLC-1720) integrated into the SH arm. To ensure the stability of the interferometer, a phase-locking system is utilized, relying on spatial interference patterns produced by a continuous-wave (CW) laser at 635 nm. This CW laser propagated collinearly with the paths of the two-color laser beams. A CCD camera was employed to capture the interference fringes generated by the CW laser upon recombination of the two beams as displayed in Fig. 4.4A-B, showing the intensity integrated spectrum and camera image, respectively. Any fluctuations in the relative path length between the two arms, which could be caused by factors like air currents or mechanical vibrations, were detected as shifts in these interference fringes (see orange curve in Fig. 4.4C). Such variations were then finely adjusted using a piezo-driven translation stage (PZT) in the FW arm within an active feedback loop. This precise adjustment not only allowed us to finely control the relative phase ( $\phi$ ) between the two-color components but also mitigated any unwanted fluctuations in the relative optical path length between the FW and SH arms ensuring a phase stability on the order of 20 mrad as shown in Fig. 4.4.

The field intensities of the FW and SH pulses at the interaction point were calibrated separately. We achieved this by measuring the pulse duration with a frequency-resolved optical gating (FROG) setup. Firstly, to characterize the pulse duration of the FW ( $\omega$ component) at 2 µm, we utilized the FROG setup based with third-order harmonic generation. This process involved the interaction of the laser pulse with a thin glass slide, which induced third harmonic generation at the surface. Secondly, to characterize the



Figure 4.4: (A) The integrated signal along the vertical direction of the interferometric fringes produced by a 635 nm diode laser as shown in (B). (C) The phases extracted from the interferometric fringes, both without (orange) and with (purple) active phase stabilization.

pulse duration of the SH frequency (2 $\omega$  component) at 1 µm, we employed FROG based on second-order harmonic generation. This technique utilized a beta-barium borate (BBO) crystal with a cut angle at 29.2° to generate the second harmonic signal. Additionally, the transverse beam profile was characterized using the knife-edge method. For the linear two-color setup, the measured intensities were ~ 2.4 × 10<sup>12</sup> W/cm<sup>2</sup> for the FW and ~  $6.0 \times 10^{13}$  W/cm<sup>2</sup> for the SH pulses. In the case of the bicircular two-color setup, the measured intensities were approximately ~  $4.0 \times 10^{12}$  W/cm<sup>2</sup> for the FW and ~  $1.0 \times 10^{14}$  W/cm<sup>2</sup> for the SH pulses.

**NanoTRIMS Setup** The setup is described in detail in Chapter 3. In particular, the phase-controlled tailored two-color laser pulses were focused inside the nanoTRIMS chamber using a concave mirror with a focal length of 75 mm to interact with the aerosolized beam of  $SiO_2$  nanoparticles. The nanoparticles were dispersed in pure ethanol with a concentration of 1 g/L and aerosolized using argon gas under atmospheric conditions. In the focus, photoionization of the nanoparticles lead to the generation of electrons and ions, and molecular dissociation of adsorbate molecules present on the nanoparticle's surface. The resulting charged molecular fragments, consisting of electrons and positive ions, were accelerated by a uniform electrostatic field of approximately 198 V/cm. This field directed the fragments toward their respective detectors, positioned on opposite sides of the spectrometer.

## 4.3 Experimental results

#### 4.3.1 Phase-calibration using argon

In the experiment, the relative phase between two color laser pulses was calibrated using the phase-dependent ionization of Argon atoms under identical conditions. Fig. 4.5A



Figure 4.5: (A) The measured momentum distribution of ejected  $Ar^+$  ions along the polarization axis (y-axis) for varying phases. (B) Phase-dependent directional preference of the  $Ar^+$  ions, displayed as asymmetry of this directional emission.

displays the measured momentum of argon ions  $(Ar^+)$  produced by the single ionization of argon atoms in the y-direction. By exploiting the distinct preferences of ejected  $Ar^+$  ions in positive, along +y  $(p_{y+})$  or negative, along -y  $(p_{y-})$  directions along the polarization axis at specific phases (0 and  $\pi$ ), we measured the asymmetry  $((p_{y+} - p_{y-})/(p_{y+} + p_{y-}))$  in this directional preference across different phases. Comparing this measured asymmetry with the already established results [94] for  $Ar^+$  ion ejection under varying phases allowed us to assign the absolute value of the relative phase between the laser pulses as shown in Fig. 4.5B. This method offers an efficient way to calibrate phase for multi-color laser experiments.

#### 4.3.2 Controlling proton emission with linear two-color pulses

The precise manipulation of relative phase in two-color laser pulses offers a mechanism to finely tune the near-field enhancement on dielectric silica nanoparticles' surfaces. In the context of linear two-color pulses, the near-field enhancement spatially assumes a dipolelike profile as shown in Fig. 4.6A and oscillates concerning variations in the relative phase  $(\phi)$  depicted in Fig. 4.6B with  $\phi = 0$  and Fig. 4.6C with  $\phi = \pi$ . This oscillation pattern correlates closely with the orientation of the maximum intensity of the driving fields shown in Fig. 4.1.

By leveraging the interaction between relative phase and near-field enhancement, this section aims to illustrate the capacity of phase-controlled, linearly polarized two-color laser pulses to influence proton emission from nanoparticle surfaces measured via reaction nanoscopy. Figure 4.6D displays the phase-integrated proton momentum distributions, in the  $p_x = 0$  plane, obtained from the dissociative ionization of the adsorbate molecules from the surface of  $300 \,\mathrm{nm} \,\mathrm{SiO}_2$  nanoparticles. Figure 4.6G shows the simulated proton momentum distribution resembling the corresponding measured proton momentum distribution. To ensure the accuracy of the results, we only selected ionization events coinciding with a strong electron channeltron signal  $(|p_u| < 35 \text{ a.u.})$  to minimize proton signals originating from the background gas. Figures 4.6E and 4.6F demonstrate distinctive phase-dependent oscillations in proton momentum distributions along the laser's polarization direction (the  $p_{y}$ -axis) as we varied the relative phase  $\phi$  from 0 to  $\pi$ . These oscillations mirror the corresponding up-and-down patterns observed within the near-field distributions of phasecontrolled linear two-color pulses (cf. Fig. 4.1C and 4.1D). This correlation underscores the direct link between the modulation in the near-field enhancement pattern and the subsequent directional variations in emitted protons. It elucidates how laser fields, governed by phase control, influence the dynamics of ion emission from nanoparticle surfaces in linearly polarized two-color fields. Figures 4.6H and 4.6I illustrate the corresponding simulated proton momentum distributions.

To enable more quantitative analysis, we introduced an asymmetry parameter  $A(\text{KE}, \phi)$ , which is a function of both the proton kinetic energy (KE) and the laser phase  $\phi$ . By tailoring the phase between the two-color components of the laser pulses, different regions on the nanoparticle surface experience varying degrees of field enhancement which translates into a differential photodissociation yield based on the relative phase difference. The asymmetry parameter is a mathematical representation used to quantify the asymmetry observed in the proton momentum angular distributions. The asymmetry parameter characterizes the directional preference or deviation from isotropy in the emitted proton distribution. It is defined as:

$$A(\mathrm{KE},\phi) = \frac{Y_{up}(\mathrm{KE},\phi) - Y_{down}(\mathrm{KE},\phi)}{Y_{up}(\mathrm{KE},\phi) + Y_{down}(\mathrm{KE},\phi)}.$$
(4.3)

The induced asymmetry observed in ion emission directly arises from the effects of phase-controlled near-field enhancements as described earlier. Figure 4.7A illustrates the observed asymmetry in proton emission, showcasing the relationship between the relative phase of the two-color linear pulses and the kinetic energy of measured protons, specifically for 300 nm SiO<sub>2</sub> nanoparticles. This two-dimensional depiction presents the comparison between the number of protons exhibiting positive longitudinal momentum and those displaying negative longitudinal momentum along the laser polarization direction of the combined linear two-color pulses. The energy-integrated asymmetry curve of 300 nm SiO<sub>2</sub> nanoparticles is shown in Fig. 4.7B along with the one measured for 600 nm SiO<sub>2</sub> nanoparticles compared to the background proton emission shown as green dots in the same figure. It was found that the emission of protons from nanoparticle surface is highly influenced by the relative phase,  $\phi$  while its dependence on KE was comparatively weak.



Figure 4.6: (A) Phase-integrated near-field enhancement around a 300nm SiO<sub>2</sub> nanoparticle with linearly polarized two-color (2 µm and 1 µm) fields where the polarization of the laser fields is along the *y*-direction. The near-field pattern is observed to align with the maximum of the electric field of the two-color phase-controlled pulses shown for  $\phi = 0$  in (B) and  $\phi = \pi$  in (C). (D, E, F) show the corresponding measured proton momentum distributions whereas (G, H, I) depict the simulated proton momentum distributions corresponding to the respective conditions.



Figure 4.7: (A) Measured asymmetry in proton emission as a function of the relative phase delay ( $\phi$ ) between linear two-color pulses and the measured KE for 300 nm SiO<sub>2</sub> nanospheres (**B**) Comparison between the measured KE-integrated asymmetry in the proton emission from 300 nm, 600 nm SiO<sub>2</sub> nanospheres and the background (**C**) Simulated KE-integrated asymmetry in proton emission for 300 nm (orange curves) and 600 nm (blue curves) SiO<sub>2</sub> nanospheres.

Furthermore, differences in the exhibited asymmetry in proton emission is observed based on the nanoparticle size. The nanoparticle size effects on the proton emission from the two-color phase-controlled pulses are discussed in the next section in detail. The simulated asymmetry curves for these different sizes are shown in Fig. 4.7C as a function of the relative phase delay between the two-color pulses, where the asymmetry curve for 300 nm nanoparticles demonstrates a high degree of reproducibility but deviates from the measured curve for 600 nm nanoparticles. The cause might be the simplicity of our theoretical modeling used to simulate the phenomena as discussed in the theoretical results section later in this chapter.

#### Nanoparticle size-dependence

The effect of the two-color field on the proton emission is also measured for 600 nm SiO<sub>2</sub> nanospheres as shown in Fig. 4.7B. The size of the nanoparticle with respect to the laser wavelength plays a critical role in the laser-nanoparticle interaction and determining the distribution and strength of the near-field enhancement around the nanoparticle surface. For spherical nanoparticles, the degree of near-field enhancement on an nanoparticle exposed to a laser field can be characterized by the dimensionless Mie parameter, defined as  $\rho = \pi d/\lambda$ , where d is the sphere's diameter and  $\lambda$  is the irradiation wavelength.

The Mie parameter is a crucial factor that characterizes the interaction between light and spherical particles highlighting the transition between different scattering regimes based on the relationship between nanoparticle size and incident wavelength. When the nanoparticles are much smaller than the incident wavelength ( $\rho < 1$ ), they demonstrate a dipole-like near-field distribution (Fig. 4.8A) with maximum enhancement aligned along the laser polarization direction. As the nanoparticle size increases and the Mie parameter is of the order of unity or larger ( $\rho \geq 1$ ), higher-order multipole modes are excited, lead-



Figure 4.8: Spatial distribution of the near-field enhancement pattern in the laser propagation-polarization (x - y) plane for different conditions as obtained from Mie simulations (**A**) 300 nm SiO<sub>2</sub> nanosphere with the fundamental laser wavelength at 2 µm. (**B**) 600 nm SiO<sub>2</sub> nanosphere with the fundamental laser wavelength at 2 µm. (**C**) 300 nm SiO<sub>2</sub> nanosphere with the second harmonic at 1 µm. (**D**) 600 nm SiO<sub>2</sub> nanosphere with the second harmonic at 1 µm.

ing to a shift in the region of maximum field enhancement towards the direction of light propagation (Fig. 4.8B-D).

This effect is especially pronounced when employing linearly-polarized two-color laser pulses. It becomes particularly evident when interacting with nanoparticles of sizes comparable to the laser wavelength in the case of fundamental wave ( $\omega$ ) and its second harmonic ( $2\omega$ ). The near-field distributions of the  $\omega$  and  $2\omega$  spectral components showcase distinct spatial profiles, resulting in the spatial separation of the regions of maximum field intensity, or "hot spots" as depicted in Figure 4.8A, C for a 300 nm diameter SiO<sub>2</sub> sphere, illuminated by the fundamental (Fig. 4.8A) and second harmonic (Fig. 4.8C) fields at 2 µm and 1 µm, respectively. For the 300 nm nanoparticles displayed in Figure 4.8A, a notable alignment is observed where the hot spots coincide predominantly along the polarization vector of the laser field. In contrast, the 600 nm nanoparticles exhibit distinct disparities in the positioning of the hot spots concerning the  $\omega$  (Fig. 4.8B) and  $2\omega$  (Fig. 4.8D) spectral components, particularly noticeable at the rear of the sphere in the laser propagation direction (see Fig. 4.8D). These variations are a consequence of the field propagation effects induced by variation in the Mie parameter inherent to the two spectral components, leading to a gradual



Figure 4.9: Measured phase-integrated proton momentum distribution in the propagationpolarization (x - y) plane for (**A**) 300 nm and (**C**) 600 nm SiO<sub>2</sub> nanoparticles. Measured proton momentum distribution shown in the  $p_x = 0$  plane, i.e., integrated in the propagation direction for (**B**) 300 nm and (**D**) 600 nm nanoparticles.

shift of the area exhibiting maximal field enhancement in the direction of propagation of the laser. It's intriguing to observe that nanoparticles with a size of 300 nm interact with a laser wavelength of 1  $\mu$ m in a manner analogous to 600 nm nanoparticles interacting with a wavelength of 2  $\mu$ m (see Fig. 4.8B,C). This equivalence arises because both scenarios exhibit the same Mie parameter, indicating a similarity in the scattering and absorption phenomena despite the differences in the nanoparticle size and incident laser wavelength.

The variations in the near-field enhancement pattern due to size-dependent effects result in distinct proton momentum distribution for  $300 \,\mathrm{nm}$  and  $600 \,\mathrm{nm}$  sized SiO<sub>2</sub> nanoparticles as illustrated in Fig. 4.9. The proton emission in the laser propagation-polarization (x-y) plane depicts the field-propagation effects observed in the near-field enhancement being translated to a front side emission of protons in the laser propagation direction with the 600 nm nanoparticles (Fig. 4.9A, C), whereas the 300 nm nanoparticles still follow a nearly dipolar proton emission (Fig. 4.9B, D). This linear control becomes more apparent when the phase-dependent yields are plotted against the angular distribution of proton momentum. Figure 4.10 shows the phase-dependent angular distribution of proton emission observed for both, 300 nm and 600 nm nanoparticles. Here,  $\Theta_{xy}$  is defined as.  $\Theta_{xy}$ =  $\arctan(p_x/p_y)$ . The angular distribution yields phase-dependent oscillations for both 300 nm and 600nm nanoparticles. When comparing the angular distributions of 300 nm nanoparticles in Fig. 4.10A with those of 600 nm nanoparticles in Fig. 4.10D, a clear distinction is visible in the phase-integrated curves. This difference arises from the change in nanoparticle size, leading to an increase in emission yields from the rear-side of the 600 nm nanoparticles, between the two dipolar peaks, as anticipated. Figures 4.10(B, E) display the 2D spectrum of the measured phase-dependent yields, illustrating the angular distribution of proton momentum for 300 nm nanoparticles and 600 nm nanoparticles, respectively. These experimental findings are complemented by simulation results presented in Fig. 4.10(C, F) for both nanoparticle sizes. We note that proton emission tends to concentrate around the poles of the nanospheres aligned with the laser polarization direction for the 300 nm nanoparticles. Due to the highly nonlinear nature of strong field-induced dissociation yields, distinct oscillations are more readily observed in both positive and negative directions along the laser polarization. Conversely, a shift in the emission direction is noticeable with the 600 nm nanoparticles, attributed to size-dependent effects in the nearfield enhancement. Consequently, the proton dissociation hotspots become more visible along the laser propagation direction.

This difference observed in the proton emission due to field-propagation effects for nanoparticles of varying sizes is reflected in the resulting asymmetry measurements. This is evident between nanoparticles sized at 300 nm and 600 nm as observed in the experimental results. For the 600 nm particles, the near-field hot spots originating from the  $\omega$  and  $2\omega$ components of the two-color pulses exhibit a lesser degree of spatial overlap. Consequently, this leads to a less pronounced control over the proton emission phase (approximately 50%) compared to the substantial control observed (around 90%) for the 300 nm particles. This disparity in the degree of phase control is highlighted in Fig. 4.7B quantified by the asymmetry parameter. The 300 nm nanoparticles showed a very clear up-and-down emission of protons from the poles of the spherical nanoparticle with the angular distribution localized



Figure 4.10: Near-field propagation effect in phase-controlled proton emission. (A) Measured normalized phase-integrated proton yield as a function of the emission angle in the laser propagation-polarization (x - y) plane for 300 nm and (B) Measured and (C) simulated angular,  $\Theta_f^{xy}$  and phase  $\phi$  resolved proton emission for 300 nm SiO<sub>2</sub> nanoparticles. (D-E) The same characteristics as described in (A-C) respectively, illustrated for 600 nm nanoparticles.

mainly around  $\pm 90^{\circ}$ , which is responsible for the high asymmetry observed in this case. While the emission of protons in the direction of laser propagation shifts the maximum around  $\pm 70^{\circ}$  with increase in emission between the peaks lowering the resulting asymmetry along laser polarization for 600 nm nanoparticles.

# 4.3.3 Two-dimensional control of proton emission with bicircular two-color pulses

Employing two-color bicircularly polarized laser pulses revealed a shift towards more intricate phase- and helicity-dependent semilunar (Fig. 4.11A) and trefoil (Fig. 4.11D) near-field patterns, originating from co-rotating and counter-rotating two-color fields, respectively. The bicircular two-color laser pulses steer the laser-induced near-field maximum in two dimensions, i.e., in the plane spanned by the laser polarization axes. For bicircular two-color laser pulses, the relative phase  $\phi = 0$  assumes particular significance within the configurations of counter- or co-rotating fields, dictating their specific alignments and resulting laser field structures (see Fig. 4.2). As evident from the findings of phase-controlled linear two-color pulses, the direction of proton ejection in tailored waveform laser fields is found to closely align with the peak of the electric field. Consequently, we can calibrate the relative phase,  $\phi$ , by analyzing the measured proton angular distributions for the bicircular fields in the polarization plane. In the case of the trefoil laser field configuration formed by counter-rotating fields, setting the relative phase  $\phi$  to zero indicates a phase relationship where one of the three lobes of the trefoil-shaped field precisely aligns along the y-axis. Conversely, in the semilunar configuration involving co-rotating fields, a relative phase  $\phi = 0$  signifies a phase relationship where the peak of the semilunar laser field aligns parallel to the y-axis. Therefore, setting the relative phase  $\phi = 0$  within these counter- or co-rotating field configurations establishes a reference point where the various components of the laser field align in a specific manner determining the characteristic shapes and spatial arrangements of the optical hotspots around the nanoparticle surface.

Figures 4.11B and 4.11E display the measured momentum distributions of protons ejected from a 300 nm nanoparticle in the polarization plane with  $\phi = 0$  for co-rotating and counter-rotating two-color fields, respectively. The semilunar pattern seen in proton momentum distributions (Fig. 4.11B) mirrors the semilunar-shaped near-field configuration (see Fig. 4.11A) produced by co-rotating fields in the bicircular two-color pulse setup. Setting the relative phase  $\phi$  appropriately to induce this semilunar field results in a corresponding semilunar pattern in the proton emission distributions. Conversely, trefoil pattern observed in the proton momentum distributions (Fig. 4.11D), the distinct three-lobed shape closely resembles the trefoil-shaped near-field distribution (Fig. 4.11D) induced by counter-rotating fields in the bicircular two-color pulse configuration. The observed findings imply that by carefully adjusting the relative phase  $\phi$  between counterrotating components, we can precisely control and align proton emission patterns with the corresponding trefoil-shaped field structure. Similar to the semilunar pattern, the trefoilshaped proton momentum distributions in their orientation and intensity



Figure 4.11: Near-field enhancement pattern around 300 nm SiO<sub>2</sub> nanoparticles with (A) co-rotating bicircular fields with the relative phase difference,  $\phi = 0$ . (B) The corresponding measured and (C) simulated proton momentum distribution in the polarization  $(p_x = 0)$  plane. D-F The traits outlined in (A-C) are mirrored for counter-propagated bicircular fields, respectively.

as the laser phase  $\phi$  undergoes continuous modulation, indicative of the control over proton emission in alignment with the changing trefoil near-field structure.

The observed trefoil and semilunar patterns in the proton momentum distributions, which mirror the induced near-field distributions by bicircular two-color pulses, highlight a direct correlation between the laser-induced near-field configurations and the resultant proton emission characteristics within the polarization plane defined by the bicircular pulses. This direct correspondence underscores the significant impact of laser field configurations on the spatial control of proton emission from the nanoparticle surfaces within the 2D plane spanned by their polarization axes. This correlation demonstrates the capability of precisely manipulating and controlling proton emission directions in two dimensions by modulating the relative phase and structure of the bicircular two-color laser fields. The observed minor asymmetry in the proton distribution along the z-axis (Fig. 4.11E) can be attributed to observed reduction in the detector's efficiency along that direction. This reduction affects ions arriving later within a mass peak, particularly those hitting the detector within the recovery time of the microchannel plate. Protons, being the predominant ion species emitted from the nanoparticle surface in our experimental setup, are highly affected by this phenomenon. This asymmetry becomes particularly noticeable when ions are emitted along the z-axis, which corresponds to the time-of-flight direction.



Figure 4.12: Measured 2-D asymmetry patterns of proton emission in the plane of polarization for counter-rotating bicircular pulses at different relative phases ( $\phi$ ).

The observed phase-dependent asymmetry in the measured proton distribution can be further elucidated through a more quantitative analysis of the two-dimensional proton emission control using the asymmetry parameter. This parameter, denoted as  $A(p_y, p_z, \phi)$ , is calculated using the measured proton yield in the momentum distribution in the laser polarization plane  $(p_y - p_z)$  and the relative phase  $\phi$  of the bicircular two-color pulses. The asymmetry parameter is defined as

$$A(p_y, p_z, \phi) = \frac{Y(p_y, p_z, \phi) - Y(-p_y, -p_z, \phi)}{Y(p_y, p_z, \phi) + Y(-p_y, -p_z, \phi)},$$
(4.4)

where  $Y(p_y, p_z, \phi)$  represents the measured proton yield at momentum  $p = (p_y, p_z)$  and the relative phase  $\phi$  of the bicircular two-color pulses. This asymmetry parameter is positive if protons are preferentially emitted with an angle  $\Theta_{yz}^f = \arctan(p_y/p_z)$ , and negative if protons are preferentially emitted with an angle  $\Theta_{yz}^f + 180^\circ$ .

Figure 4.13 and Fig. 4.12 showcase the corresponding two-dimensional asymmetry pattern of the proton momentum distributions in the y - z plane for co- and counterrotating two-color pulses for different values of the relative phase,  $\phi$ , respectively. These visualizations offer a comprehensive understanding of the proton emission characteristics, demonstrating how protons are preferentially emitted with specific angles depending on the relative phase of the bicircular two-color pulse. We observe that changing the values of the relative phase,  $\phi$  from 0 to  $2\pi$  results in a complete revolution of emission of protons around a circle in the plane  $p_x = 0$ . The changes in the 2D asymmetry patterns behaves


Figure 4.13: Measured 2-D asymmetry patterns of proton emission in the plane of polarization for co-rotating bicircular pulses at different relative phases ( $\phi$ ).

akin to a rotating fan as the laser phase  $\phi$  varies continuously, depicting the manipulation of proton emission directionality in conjunction with the changing field structure. An intriguing observation from these analyses is that despite the two-color laser pulses with different helicities having the same peak combined field intensity in the experiment, the measured asymmetry contrast in co-rotating fields (~75%) in Fig. 4.13 is notably larger than that in counter-rotating fields (~30%) in Fig.4.12). This discrepancy highlights the influence of the pulse helicity on the observed asymmetry in proton emission.

Moreover, it's noteworthy that similar spatial control can be expected for nanoparticles with a diameter larger than 300 nm, provided that the field-propagation effects remain sufficiently small. However, for nanoparticles of 600 nm, the field-propagation effect becomes noticeable. Nevertheless, since the extent of the propagation effect relies on particle properties and laser wavelength rather than the electric field's polarization, a similar phase control as in the linear two-color experiment is anticipated for the bicircular two-color case, even with 600 nm particles. The sensitivity of the near-field distribution to the relative phase and polarization of the two-color pulses paves the way for the site-specific control of near-field-driven molecular adsorbate reactions on the nanoparticle's surface.

# 4.4 Theoretical modeling and results

The electrostatic Classical Trajectory Monte-Carlo (CTMC) simulations as detailed in Chapter 2 were able to assist in the interpretation of the proton dynamics observed in this chapter. In general, the calculations involved the generation of the near-fields, the creation of static charges, the sampling of protons residing on the nanoparticle's surface, and the classical propagation of protons within the static fields generated by the charged particle to result in the final calculated proton momentum spectra, based on the details as described in Chapter 2.

In particular, the phase-dependent near-field enhancement occurring on the nanoparticle's surface were derived from finite-difference time-domain (FDTD) calculations using the software Lumerical. For two-color linearly polarized field, two "TFSF (Total Field Scattered Field)" sources with linear polarization along the y-axis served as the light source. Both the light pulses, defined by a Gaussian profile, centered around 2 µm and 1 µm respectively, with unit amplitude and a given time offset and bandwidth, were introduced simultaneously in the simulation frame. The crucial element was the phase difference between the two colors, controlled via the "Phase" parameter to influence the near-field pattern. The calculations were performed on a grid with a spacing of  $5 \,\mathrm{nm}$  for  $300 \,\mathrm{nm}$  nanoparticles and 10 nm for 600 nm nanoparticles. The near-field distribution was recorded using the frequency-domain field monitor placed around the simulation region, after running the simulation and ensuring convergence through Lumerical's checks. To quantify the enhancement, the near-field enhancement factor was calculated by dividing the near-field intensity by the normalized incident light intensity considering both the components of the two-color fields. The result for the linear two-color pulses is shown in Fig. 4.6A-C as described earlier, for phase-integrated (Fig. 4.6A) and phase-specific scenarios (Fig. 4.6B-C) respectively. For the bicircular two-color fields, four different TFSF sources were introduced simultaneously, as each color is represented by two distinct components along y- and z-directions for circuclarly polarized fields as described in Eq. 4.2. Light source exhibiting circular polarization possesses two orthogonal electric field components with identical amplitudes and a relative phase difference of  $\pi/2$  radians. The key to bicircularity lies in the relative phase shift between the two color components. We used the "Phase" parameter for each source to introduce this additional phase difference beyond the individual 90° shifts within each color. The specific value of this relative phase shift determines the handedness (leftor right-handed) of the resulting bicircular field. For instance, for generating a left-handed (counter-propagating) bicircular field the following steps were implemented. Each color component, with its distinct wavelength  $(2 \,\mu m, 1 \,\mu m)$ , was defined by its injection axis (y, y)z), propagation direction (along x), unit amplitude, and initial phase ( $\phi_1, \phi_2$ ). To achieve circular polarization within each color, we set their polarization angles to  $90^{\circ}$  (s) and  $0^{\circ}$  (p), respectively, and utilized the "Theta vs wavelength plot" to introduce a 90° phase shift for the orthogonal electric field component. For instance, the key to left-handed bicircularity was the carefully controlled relative phase difference  $(\phi_1 - \phi_2)$  between the colors, with a positive value for color 2 ( $\phi_1 > \phi_2$ ) ensuring the desired handedness. The near-field distribution obtained via numerical for co-rotating and counter-rotating bicircular fields are

shown in Figs. 4.11A and 4.11D for  $\phi$  ( $\phi_1 - \phi_2$ ) = 0, respectively.

Following the detailed steps outlined in Chapter 2, we utilized the extracted field enhancement distribution scaled by the experimental intensities to generate positive surface charges on the nanoparticle surface via ADK ionization rate using the ionization potential,  $I_p = 10.2 \text{ eV}$  for SiO<sub>2</sub> [95]. The number of static surface charges was introduced as a free parameter, with its value determined by fitting against the measured proton momentum distribution for each configuration. Proton distributions on the nanoparticle's surface were sampled from the simulated spatial distribution of molecular dissociative ionization probability using the power-law function dependent on laser intensity,  $I^n$ . In this case, a power order of n = 13 accounted for the combined contributions of the two-color laser pulses. The spatial arrangement of molecules on the nanoparticle surface was mathematically modeled by a radial Gaussian distribution function. This function was centered at the nanoparticle's surface with a standard deviation of  $\sigma = 10$  nm. It's noteworthy that the laser intensity employed for proton generation was assumed to be far below the saturation regime, which was a justifiable assumption considering the low proton rate, amounting to less than one proton per laser shot in the experiment. Given the highly nonlinear scaling of proton yield with laser intensity in the non-saturated regime, the simulations did not account for focal-volume averaging effects. To generate momentum spectra, the sampled protons were then propagated classically within the static field generated by the positive charges residing on the surface of the nanoparticle. Multiple sets of sampled charges were simulated to ensure the convergence of the final momentum distribution.

As illustrated in Figs. 4.6G-I, the momentum distributions of protons emitted from nanoparticles under the influence of linearly polarized two-color pulses (Fig. 4.6G), as well as the characteristics of the two-color phase dependency (Fig. 4.6H-I), are qualitatively replicated by the CTMC simulations, aligning well with the experimental parameters. Furthermore, the simulation results for 300 nm and 600 nm particles effectively reproduced the attributes of field-propagation effects on the angular distributions, as depicted in Figs. 4.10A, D (dashed lines), and Figs. 4.10C, F, respectively. It's worth noting that the difference in the amplitude of the asymmetry curves (see Fig. 4.8C) between the 300 nm (orange dashed curve) and 600 nm (blue dashed curve) particles is less pronounced in the simulations compared to the measurements, we attribute this discrepancy to the model's inherent simplicity. Nevertheless, the qualitative agreement between the simulations and experimental observations regarding the two primary characteristics of asymmetry, i.e., the preferential proton emission along the maximum of the asymmetric optical fields, as well as the somewhat greater asymmetry amplitude for smaller nanoparticles, is indeed noteworthy. Most critically, our theoretical model also qualitatively reproduces the phasedependent trefoil and semilunar structures and asymmetries within proton momentum distributions measured with co- and counter-rotating bicircular two-color laser pulses, as delineated in Figs. 4.11C and 4.11F for  $\phi = 0$ , respectively.

# 4.5 Mapping between proton momentum and birth positions

Previous research on optical control of particle emission dynamics in laser-nanoparticle interactions has predominantly concentrated on electron emission from nanosystems, as evidenced by various studies [12, 59, 92, 60, 51, 96, 57, 97]. These investigations mainly focused on manipulating rapid photoemission processes, which are primarily influenced by the combined fields near the nanoparticle's surface. These fields include the dielectrically enhanced near field generated by incident laser pulses and the surface trapping potential originating from released electrons and residual ions [12, 59, 55, 58]. However, in this chapter, our focus shifts towards ion emission dynamics, specifically the behavior of significantly heavier protons, due to their distinct response mechanisms. While electrons are primarily governed by the near field dynamics induced by the laser-nanoparticle interaction, protons exhibit much slower dynamics driven primarily by the repulsive Coulomb force exerted by the positively charged nanoparticle after the photoemission of electrons.

Our approach stands out for its ability to tailor the near-field induced dissociative ionization yields of protons using phase-controlled linear and bicircular two-color laser pulses. The high nonlinearlity of the strong-field ionization of the nanoparticle surface allows for the generation of precise anisotropic charge distributions, facilitating the manipulation of charge-driven directional proton emission. While electron emission tends to maintain directionality primarily for near-cutoff electrons [12, 60, 59], the proton emission observed in this chapter exhibited phase- and polarization-dependent characteristics for the majority of emitted protons. Consequently, proton emission serves as a sensitive probe for observing local reaction yields on the nanoparticle surface manipulated by tailored laser fields. To precisely manipulate this spatial control over surface reaction yields, it's crucial to explore the mapping relationship between the initial dissociation yield landscape on the surface and the measurable final proton momentum distributions obtained via reaction nanoscopy.

To illustrate this correlation, we plotted the relationship between the simulated angular distribution of the proton birth positions  $(\Theta_b^{yz})$  and the final momentum distribution  $(\Theta_f^{yz})$  of proton emission induced by a counter-rotating bicircular two-color laser pulse at  $\phi = 0$  as depicted in Fig. 4.14A. While in the case of radial emission, the angle-correlation distribution should strictly follow the black dashed diagonal line, closer examination of the correlation map reveals angle-dependent wiggle structures near the birth surface positions corresponding to the minimum  $(\Theta_b^{yz}=60^\circ)$  field enhancement. These structures are attributed to inhomogeneous charge distributions induced by the near field on the nanoparticle surface. The surface positions in proximity to the points of maximum field enhancement (hot spots) generate more positive charges due to the higher field intensity. Consequently, for protons born near the hot spots, radial emission predominates due to the high symmetry of the local charge distribution, facilitating a one-to-one mapping between birth and final angles as shown in Fig. 4.14B. For protons created at surface positions away from the hot spots, the additional Coulomb force from the higher local charge at the hot spots results in a deflection of the actual emission direction to a larger angle as shown



Figure 4.14: (A)The correlation map of the simulated proton birth positions,  $\Theta_{yz}^b$ , and final angular distribution,  $\Theta_{yz}^f$  of proton momentum distribution for counter-rotating bicircular fields at  $\phi = 0$ . B-C Zoom in the correlation map between proton birth angle between -30° to 30° and 60° to 90° respectively (D) The difference between the angular distribution of final proton momentum distribution and birth positions,  $\delta \Theta_{yz}$  as a function of proton birth positions  $\Theta_{yz}^b$  and (E) the birth-angle integrated distribution. The red curve shows the Gaussian fit to the data.

by the wiggle structure in Fig. 4.14C.

To quantitatively measure the deviations between the birth and final angles, we calculated their angle difference, denoted as  $\delta \Theta^{yz} = \Theta_b^{yz} - \Theta_f^{yz}$  for each proton trajectory. The scatter plot of  $\delta \Theta_b^{yz}$  as a function of the birth angle is displayed in Fig. 4.14D. By fitting the angle-integrated  $\delta \Theta^{yz}$  distributions presented in Fig. 4.14E, we obtained a full-width half-maximum (FWHM) of  $\delta \Theta_{FWHM}^{yz} \sim 9.8^{\circ}$ , signifying a relatively small mean value of angle deviation, approximately 4.9°, considering both left and right deviations from the diagonal. Despite the existence of small wiggle structures in the correlation map, the overall distributions of the angle correlation in Fig. 4.14A feature an almost diagonal shape with an angle correlation coefficient of ~0.996. This observation implies a near-one-to-one mapping between birth and final angles, equivalent to the mapping between birth position and the measured angular momentum distribution of protons emitted from the nanoparticle surface.

The comparison of the presented mapping to that reported using rescattered electrons near their energetic cutoff [12, 60, 59, 58] provides valuable insights. Rescattered electrons tend to exhibit a broader distribution, primarily due to collisional dynamics, and their yield decreases significantly as they approach the cutoff energy. This leads to a considerably lower correlation between the birth position and final emission angles, resulting in non-correlated emissions at lower photoelectron energies. In contrast, when it comes to the emission of heavier protons, the correlation between birth-to-final angles is orders of magnitude higher as their movement is primarily driven by the repulsive Coulomb forces



Figure 4.15: Normalized 2D spectra of phase-dependent final angular proton momentum distribution (A) simulated and (B) measured, obtained using bicircular counter-rotating bicircular two-color laser pulses. (C) Phase-of-phase,  $\phi_{PP}$  spectra retrieved from the simulated proton emission angle (blue crosses) and measured proton emission angle (red dots).

of the static positive charges on the nanoparticle surface, and it remains independent of the ion energy.

The control over spatial variability of proton emission from the nanoparticle surface is well-demonstrated via examining the phase-dependent angular distribution of protons with counter-rotating bicircular two-color laser pulses. Figure 4.15A illustrates the phasedependent simulated angular distribution of protons in the  $(p_y, p_z)$  plane of a counterrotating bicircular two-color laser pulse, while Fig. 4.15B depict the experimental variation measured as

$$Y_{Norm}(\Theta_{yz}^{f}, \phi^{i}) = \frac{Y(\Theta_{yz}^{f}, \phi_{i})}{\frac{1}{N} \sum_{\phi_{i}=0}^{\phi_{N}=2\pi} (\Theta_{yz}^{f}, \phi_{i})}.$$
(4.5)

Here,  $Y(\Theta_{yz}^f, \phi_i)$  represents the collected proton yields at the final emission angle  $\Theta_{yz}^f$ for laser phase  $\phi$ , and N is the total number of scanning steps over  $2\pi$ . The diagonal structures in this plot indicate the rotation of proton momentum lobes with increasing laser phase.

To quantitatively extract the mapping relation between the continuously varied relative phase and the proton emission angle, we extracted the "phase-of-phase" (PP) spectra, denoted as  $\phi_{PP}$ . This was achieved by fitting a cosine function,  $Y_{Norm}(\phi) = Y_0 + A_0 \cos(\phi + \phi_{PP})$ , for each angle  $\Theta_{yz}^f$ , where  $Y_0$  represents the background count,  $A_0$  is the phase contrast, and  $\phi_{PP}$  signifies the changes in laser phase concerning  $\phi = 0$ . In Fig. 4.15C, when the emission angle  $\Theta_{yz}^f$  varies by 360°, the phase  $\phi_{PP}$  changes by  $6\pi$  in total. This corresponds to a proton emission angle that rotates from -180° to 180° as the relative phase  $\phi$  varies from 0 to  $6\pi$ . The results, as indicated by red solid circles, align closely with the data points retrieved from simulations (blue crosses). The consistency between the experimental and simulated data points in the retrieved phase-of-phase spectra and considering the relationship between the angle-resolved proton birth position and final momentum distribution established via the simulations earlier show that the proton birth



Figure 4.16: The measured two-dimensional asymmetry patterns of proton momentum distribution shown in polar coordinates in the (y - z) plane, i.e.,  $p_r$  vs  $\Theta_{yz}^f$  with (**A**)  $\phi = 0$  and (**B**)  $\phi = 0.125\pi$ , respectively. The purple dots show radial momentum-integrated proton angular distribution fitted using sinusoidal curves shown in black. The top-blue axis denotes the corresponding change in the relative positions of the proton emission.

angle can be controlled using the laser phase. This is achievable by adjusting the laser phase through a nearly one-to-one mapping between the phase  $(\phi)$  and the birth angle  $(\Theta_{uz}^b)$  measured in radians and degrees, respectively, given by

$$\Theta_{uz}^{b}(\phi) = (360^{\circ}/6\pi)\phi - 180^{\circ}.$$
(4.6)

This phase control of the birth angle on a nanosphere can be directly translated to the spatial birth position control on the nanoparticle surface using the formula

$$S_R^{yz}(\phi) = \pi \left(\frac{\Theta_{yz}^b(\phi)}{360^\circ}\right) d,\tag{4.7}$$

where d represents the nanosphere diameter. Within the laser polarization plane of a counter-rotating bicircular two-color laser pulse, when the laser phase  $\phi$  varies by  $6\pi$ , the proton birth position on the surface can be changed from  $-\pi d/2$  to  $\pi d/2$ . Therefore, by combining the angle-to-angle, angle-to-phase, and phase-to-position mapping relations, the spatial control of molecular reaction yields on the nanoparticle surface via laser phase can be implemented with nanoscopic resolution. This resolution depends on the nanoparticle's diameter, d and the step size of the adjustable relative laser phase,  $\phi$ .

Figures 4.16A and 4.16B show the measured two-dimensional asymmetry pattern of the proton momentum distribution in polar coordinates of the  $(p_y, p_z)$  plane. As the phase  $\phi$  varies from  $0\pi$  to  $0.125\pi$ , an angle shift of  $\sim 8^{\circ}$  of the near-field hot spots is observed, which is equivalent to steering the proton birth position by  $S_R^{yz} \approx 21$  nm on the surface of a d = 300 nm nanoparticle. Considering an angular resolution of approximately 4.9°, determined by the mean value of the angle deviation between the birth and final angle, the spatial resolution for surface position control can be estimated as approximately ~13 nm for the 300 nm particles.

# 4.6 Conclusion

The chapter discusses a shift in research focus from electron to ion emission dynamics in laser-nanoparticle interactions with tailored laser fields, particularly emphasizing proton behavior driven by the repulsive force from positively charged nanoparticles after electron release. Previous studies predominantly concentrated on rapid photoemission processes influencing electrons near the nanoparticle surface. However, this work delves into manipulating dissociative ionization yields of protons using tailored laser pulses. Experimental results illustrate the manipulation of proton birth positions on nanoparticle surfaces using phase-controlled two-color linear and bicircular pulses. Proton emission, unlike electron emission, displays very strong phase- and polarization-dependent characteristics, making it a sensitive probe for observing local reaction yields on nanoparticle surfaces. The study identified the relationship between initial dissociation yield landscape on the nanoparticle surface and final proton momentum distributions, revealing a nearly one-to-one mapping between birth and final emission angles of the dissociated protons. This mapping provides insights into surface reaction dynamics manipulated by laser fields. Furthermore, experiments with counter-rotating bicircular two-color laser pulses demonstrate control over the spatial variability of proton emission, showcasing the ability to steer proton birth positions on nanoparticle surfaces with nanoscopic resolution using laser phase adjustments. By establishing mappings between angle-to-angle, angle-to-phase, and phase-to-position relations, spatial control of molecular reaction yields on nanoparticle surfaces via laser phase modulation is achievable with nanometer-scale resolution. The experimental findings in conjunction with the theory results revealed an anglular shift of near-field hot spots, and the corresponding momentum distribution of protons emitted from the nanoparticle surfaces with varying laser phase. The spatial resolution for surface position control is estimated to be  $\sim 20 \,\mathrm{nm}$  for  $300 \,\mathrm{nm}$  particles, considering an angular resolution of about 8°. This chapter demonstrates the exciting potential to observe and control molecular adsorbate reactions on the nanoparticle surface with nanoscale precision using tailored laser fields. This capability may open up new avenues for understanding and manipulating chemical processes at the nanoscale level, which has significant implications for fields such as nanotechnology [98, 99], catalysis [73], and materials science. By exerting precise control over these reactions, one can potentially engineer novel materials with tailored properties and functionalities for various applications, ranging from biomedical sensing [100] to energy

conversion [101].

# Chapter 5

# Tracking surface charge dynamics on single nanoparticles

In previous studies employing reaction nanoscopy, it was shown that the non-uniform distribution of proton momentum emitted after strong-field ionization of silica nanoparticles maps out the differential reaction yield landscape across the particle's surface. This establishes a direct correlation between proton emission in real-space and the resulting proton momentum distribution [52]. Beyond its capacity for real-time differentiation of individual nanoparticles and their aggregates [63], reaction nanoscopy offers observation of the control and manipulation over the spatial distribution of reaction yields on the nanoparticle surface achieved using two-color tailored laser fields with nanoscale precision [93] as demonstrated in the previous chapter. While these observations have predominantly focused on near-field mapping, relying on the electrostatic interplay between surface charges and emitted protons, the dynamic visualization of laser-induced surface charge behavior has remained experimentally unrealized. In this chapter, we showcase how the emission of ions from the nanoparticle's surface can serve as a highly sensitive probe for capturing local surface charge dynamics in real-time. This chapter delves deeper into the research outlined in the arXiv submission [102].

# 5.1 Introduction

Understanding surface charge dynamics upon laser irradiation in nanostructures is crucial for elucidating the fundamental processes governing the interaction between light and nanomaterials. These dynamics not only provide insight into the mechanisms at play but also significantly influence the performance and functionality of nanoparticles [103]. For instance, aiming for therapeutic purpose, the surface charge density and electrostatic potential of nanoparticles determine their cellular uptake ability and interaction with other biological environments [104]. Moreover, the dynamics of surface charges, such as their diffusion, is of fundamental importance in regulating the electrostatic aggregation, manybody interactions, and particle self-assembly in colloidal science [105, 106] and biophysics [107, 108, 109, 110]. In the realm of laser-nanosystem interaction, the light-induced surface charges also play a central role in trapping-field assisted electron acceleration [12, 55], precision laser-machining [111], and laser ablation synthesis of nanoparticles [112].

Electrical surface charges on nanostructures may undergo a variety of intriguing ultrafast dynamics, such as electron scattering [12], nanoplasma expansion [13, 14], charge regulation [113, 114], and charge diffusion [115, 116, 117, 118, 119, 41, 42, 39, 40]. The fieldfree redistribution of surface charges is a fundamental non-equilibrium process relevant for many applications, such as triboelectric nanogenerators [115, 116], electrostatic separation [117, 118], and optical semiconductor engineering [119]. Despite the widely known significance of surface charges on nanostructures, a fundamental understanding about their ultrafast and nanoscopic dynamics is rather limited. Research has been conducted to characterize the surface charge generation and redistribution processes with various approaches, including atomic force microscopy [41, 42], or optical light diffraction based on the laserinduced transient grating technique [39, 40]. However, these methods either require the samples to be deposited on a substrate, which inevitably interferes with the surface charge dynamics and are technically limited in time resolution [41, 42], or have been restricted to macroscopic specimens, lacking spatial resolution [39, 40]. A profound insight into the in-situ ultrafast charge dynamics at the nanoscale is thus hardly achieved.

Turning to the field of catalysis, strategically inducing positive charges on material surfaces has emerged as a promising approach to tailor and enhance catalytic performance [25]. This process, which involves modulating a material's energy levels through the introduction of surface-bound charges, can enable the adjustment of catalytic activity. Such positive charges at the surface substantially impact the electronic structure of catalysts, leading to alterations in surface potential and, subsequently, influencing how adsorbed reactants adhere to the surface [25, 24, 54, 120]. The manipulation of surface charge states offers precise control over chemical transformations in nanoscale systems, providing unprecedented opportunities for enhancing catalytic performance. For instance, surface charge states in metal nanocrystals are found to be responsible for regulating the state of adsorbed molecules, affecting their activation, and resulting in adaptable catalytic properties [24]. Moreover, surface charges can induce and/or enhance the photochemical reactions on the nanoparticle surface, which have played a fundamental role in nano-photocatalysis research as well as astrochemistry and atomospheric science.

One effective strategy to generate surface charges on nanoparticles involves utilizing femtosecond laser pulses to induce strong-field ionization. This technique leverages the interaction of light with nanoparticles, resulting in localized electromagnetic field enhancement around their surfaces. This phenomenon significantly influences surface reactions by increasing the number of energetic charge carriers. Specifically, positive surface charges are generated on the nanoparticle surface through the release of energetic electrons [12]. The strong-field laser-nanoparticle interaction creates a nanoscale environment characterized by trapped electrons unable to escape the strong positive potential at the nanoparticle surface [55], leading to localized charge interactions that pave the way for novel reaction pathways. Recent investigations into the catalytic potential of strong-field ionized dielectric silica nanoparticles have unveiled their ability to drive bimolecular photochemi-



Figure 5.1: Schematic representation of the pump-probe technique used for probing nanoscale surface charge dynamics on  $SiO_2$  nanoparticles. We used infrared (IR) laser pulses at 2 µm wavelength as the pump pulses. These intense laser pulses are used to generate positive surface charges (depicted by blue plus signs) on the surface of a silica nanoparticle through strong-field ionization, where electrons are released (shown as green spheres blasting off) due to near-field enhancement. The positive surface charges lead to electron density delocalization away from the terminal O-H bonds at the silica surface, thereby inducing weakening of the O-H bonds. Subsequently, a probe pulse with orthogonal polarization, here the 1 µm pulses, disrupts these weakened bonds, leading to emission of protons (H<sup>+</sup>). The measured momentum distribution of emitted protons can be used as an indicator of the spatial distribution of the underlying surface charge distribution at varying pump-probe time delays.

cal reactions, leading to the formation of  $H_3^+$  from water [53]. Understanding how surface charges behave after laser irradiation aids in elucidating the underlying physical mechanisms such as surface potential alteration, reactant binding, charge transfer, and carrier dynamics. Despite the general acknowledgement of the importance of charge-mediated surface chemistry, detailed knowledge about the influence of charge dynamics on the chemical bonding of molecular adsorbates, as well as direct experimental observations, are still lacking for nanoscale systems. Direct imaging of ultrafast surface charge dynamics on isolated nanoparticles after laser irradiation, in particular, under soft irradiation conditions, is crucial for achieving such goal.

This chapter introduces a novel method for observing the real-time evolution of lightinduced surface charge distribution on individual dielectric  $SiO_2$  nanoparticles. Utilizing femtosecond pump-probe spectroscopy technique with the reaction nanoscope, we study the spatio-temporal evolution of the surface charge density. This connection is established by mapping the surface charge distribution to emission of protons from the nanoparticle surface by investigating the proton momentum distribution as a function of the time delay between the pump-probe pulses. The experimental schematic is illustrated in Fig. 5.1. Our measurements also reveal the influence of surface charge redistribution on weakening adsorbate binding on the nanoparticle surface. Through analysis of the broadening in the proton momentum angular distribution and the decay of KE in these proton emissions, we achieve a four-dimensional (4D) visualization of surface charge density dynamics in both space and time. To further understand these dynamics, we employ diffusion-model-assisted classical electrostatic simulations (d-CTMC), which provide a clear representation of the redistribution process and align well with experimental observations. Non-adiabatic quantum molecular dynamics (NAQMD) simulations elucidates the bond-weakening in the surface molecular groups induced by the presence of the surface charges and their redistribution. This exploration of surface charge dynamics offers valuable insights into fundamental nanoscale processes, contributing to the advancement of our understanding and control of nanoparticle behavior.

# 5.2 Experimental Techniques

#### 5.2.1 Pump-probe reaction nanoscopy

As depicted in Fig. 5.1, the experimental methodology involved conducting time-resolved pump-probe measurements within the NanoTRIMS apparatus. A similar optical setup to the one described in Chapter 4 involving a Mach-Zehnder Interferometer is utilized in the current measurements in the pump-probe configuration.

The laser pulses at 2 µm from the custom-built Innoslab based OPCPA system were used as the pump pulses mainly and frequency-doubled in a lithium niobate crystal to create 1 µm pulses polarized orthogonal to the input pulse for the probe arm. Selecting the orthogonaly polarized pump and probe pulses was crucial. It enabled us to differentiate how each pulse interacted uniquely with the surface of the nanoparticles, resulting in specific regions on the nanoparticle surface with different optical hotspots for every pulse. As described in detail in Chapter 4, dedicated optics including dichroic beamsplitters and polarization control elements, ensured proper separation and co-alignment of these pulses within the interferometer. The setup allowed for independent manipulation of light intensity and polarization in each arm. To control the intensity of the laser pulses, a pair of half-wave plate (HWP) and wire-grid polarizer (WGP) was used whereas the polarization was controlled using a HWP only, whenever required. The quarter-wave plate (QWP) and phase-lock active feedback loop were removed from the interferometer optics for the current experiment as only linearly polarized pulses without any phase-control were used for the time-resolved measurements.

Additionally, to optimize the pulse duration, a dispersion compensation module was integrated into each arm of the interferometer, comprising customized chirp mirrors designed by Sambit Mitra, Shubhadeep Biswas, and Vladmir Pervak. As a result, we achieved pulse durations of approximately 35 fs for the 2  $\mu$ m pulse and about 30 fs for the 1  $\mu$ m pulse. The SLC1720 delay-stage was replaced by another motorized delay stage (PI-M406.4PD) with a longer translation range to facilitate the precise control of the time delay between the pump and probe pulses upto ~300 ps. The NanoTRIMS experimental setup is detailed in Chapter 2. In short, it involved collimated laser beams focused by a concave mirror intersecting with a stream of  $SiO_2$  nanoparticles generated by aerosolization in ethanol. Different nanoparticle sizes (200 nm, 300 nm, and 600 nm) suspended in pure ethanol at concentrations of 0.1 g/l, 0.2 g/l, and 0.5 g/l respectively, were used for the measurements. The focused laser pulses interact with these nanoparticles, ejecting high-energy ions and electrons. The ion detector, including a microchannel plate stack and a delay-line detector, captured the time-of-flight and impact positions of the ions, allowing for reconstruction of their complete three-dimensional momentum distributions at variable time delays between the pump and probe pulses in a sequential manner.

#### 5.2.2 Setting up the motorized delay stage

The motorized delay stage, PI-M406.4PD, is a precision linear translation stage with a travel range of 100 mm and a minimum incremental motion of 0.25  $\mu$ m. Setting up the delay stage parameters involved defining the travel range, step size, number of steps, and step duration. For instance, to scan a delay range from -100 ps to 100 ps with a step size of 1 ps, we needed a total of 200 steps. Each step increment of 0.25  $\mu$ m corresponded to approximately ~1.67 femtoseconds delay between the pulses in the two arms. Therefore, for a 1 ps step, we needed a step size with 600 increments, equivalent to 150  $\mu$ m.

To ensure adequate statistical accuracy, we allocated a step duration of approximately 4 seconds to each step during the scanning process. Thus, one full translation of the stage required 200 steps  $\times$  4 seconds = 800 seconds, approximately 13 minutes. This process was repeated a large number of times to accumulate sufficient statistics for each step, depending on the used laser intensity.

In the experiments, we utilized various step sizes of the delay stage, starting with the minimum allowed possible delay of  $\sim 1.67$  femtoseconds, to investigate surface charge dynamics within individual laser pulse sub-cycles. However, the main interesting feature observed was the proton KE decay feature. Focusing on that, the scan range was extended to the farthest possible allowed to reach the asymptotic value of the decay curve. For the larger delays, the step size was also increased to optimize experimental efficiency by minimizing the required experimental time.

# 5.3 Experimental Results

#### Mapping Surface Charge to Surface Proton Emission

The momentum distributions of protons dissociated from the surface of a 300 nm SiO<sub>2</sub> nanoparticle by 2 µm and 1 µm laser pulses are shown in Fig. 5.2A and B, respectively. Both exhibit dipolar patterns aligning with the respective laser polarization directions: y-axis for 2 µm and z-axis for 1 µm as referenced in the lab frame. This time-independent, dipolar proton emission under separate pump and probe pulses agrees with previous findings using linearly polarized pulses [53, 52, 63] and aligns well with local near-field and



Figure 5.2: Measured proton momentum distribution along the laser polarization direction for (A) Single 2 µm pulses (B) Single 1 µm pulses (C) The time-integrated distribution of proton momentum results from the combined influence of both the pump and probe pulses in their common plane of polarization, i.e.,  $p_x = 0$ .

surface charge distributions observed with the specific laser waveforms [93]. When both pulses are introduced simultaneously at variable delays, the time-integrated proton momentum distribution produces a double-ring structure in the combined plane of polarization, i.e.,  $p_x = 0$  as shown in Fig. 5.2C. The outer ring exhibits dipolar emission in both y and z directions, mirroring observations with individual pulses (Fig. 5.2A, B) while the inner ring is attributed to the collective influence of both the pulses.

The kinetic energy (KE) spectrum of the observed protons shows a pronounced timedependent decay channel as a function of the time delay between the pump and the probe pulses, cf. Fig 5.3A. The spectrum reveals two distinct regions, characterized by proton energies falling above ~20 eV, here denoted as Region 1 and below ~20 eV denoted by Region 2 and 3 for negative and positive delays, respectively. On the positive delay side, the 2 µm pulse acts as the pump and precedes the 1 µm pulse acting as the probe whereas the roles of both the pulses are interchanged on the negative delay side. The high-energy band with a mean value of ~30 eV is essentially delay-independent. These protons predominantly originate from single-pulse processes, where either the pump or the probe beam individually triggers the formation of surface charges and subsequent proton emission. This interpretation is corroborated by examining the protons observed within the outer-ring structure in the time-integrated proton momentum distribution in the  $p_x = 0$ plane in Fig. 5.2C.

The energy region below 20 eV in Fig. 5.3A shows a clear time-dependence, where the proton KE decreases with pump-probe delay in either direction to an asymptotic energy of ~ 3 eV, within time delays of  $\pm 300 \,\mathrm{ps}$ . As compared to the previously studied low proton KE (0 ~ 3 eV) in strong-field induced Coulomb fragmentation of gas-phase H<sub>2</sub> molecules [121], the here-observed much higher initial KE of protons (~30 eV) and the time-dependent KE decay feature can be attributed to the electrostatic interactions with the positively charged nanoparticle surfaces [52]. In the time-integrated signal in Fig. 5.2C



Figure 5.3: (A) Measured proton KE spectrum as a function of time delay between 2 µm and 1 µm pulses in the pump-probe experiments. The 2 µm pulse (y-polarized) comes first for positive delays, while for negative delays the 1 µm pulse (z-polarized) comes first. (B, C) Time-integrated proton momentum distributions in the  $p_x = 0$  plane, corresponding to the delay-dependent energy decay signal for negative (Region 2) and positive (Region 3) delays, respectively.

this corresponds to the inner ring structures, which are not observed with a single pulse (compare Figs. 5.2A and B). To identify how the pump and probe pulses jointly contribute to the observed delay-dependent proton emission and the associated surface charge dynamics, we plotted the time-integrated proton momentum distributions for the positive and negative delays in Figs. 5.3B and C, respectively. Interestingly, one can observe that the proton emission pertaining to the KE decay feature is consistently predominated by a momentum distribution aligning along the polarization direction of the first-arriving pump pulse for both the positive (along y-axis) and negative (along z-axis) delays. This feature is interesting as even though the probe pulse, which initiates the proton release, is polarized perpendicular to the pump pulse. The polarization-sensitive proton emission allows us to distinctly discern the individual contributions of the pump and probe pulses in mapping the distribution of surface charge density.

The proton KE decay trend can be suitably modeled using a bi-exponential fit, represented by the equation

$$y = y_0 + A_1 \exp(-t/\tau_{\text{fast}}) + A_2 \exp(-t/\tau_{\text{slow}})$$
 (5.1)

where  $A_{1,2}$  denotes the amplitude,  $y_0$  signifies offset, and  $\tau_{\text{fast}}$  and  $\tau_{\text{slow}}$  represent the fast and slow time constants. The confidence level for the fit parameters, at 95%, yields timescales for the fast and slow KE decay processes on a 300 nm nanoparticle, approximately  $\tau_{\text{fast}} \sim (10.3 \pm 0.1)$  ps and  $\tau_{\text{slow}} \sim (70.1 \pm 1.8)$  ps, respectively. The amplitude values for the fast and slow processes, denoted as  $A_1$  and  $A_2$ , are  $\sim 20$  and  $\sim 7$ , respectively.

The bi-exponential nature of proton KE decay signifies the coexistence of two distinct timescales within the charge redistribution dynamics governing proton dissociation, providing strong evidence for a two-step process. Initially, the arrival of the first-arriving pump pulse generates positive surface charges, their distribution closely following the laserpolarization-sensitive near-fields [93]. These charges subsequently redistribute across the particle's surface, influencing the reactivity of surface-adsorbed molecules along their path. The proximity of local surface charges weakens the surface molecular bonds by redistributing electron density toward the highly positively charged nanoparticle surface. As a result, the later-arriving probe pulse, even polarized perpendicularly to the pump pulse readily induces surface molecular dissociation due to bond-weakening. This leads to the generation of protons that closely track the (re)distribution of surface charges. With the dissociation of protons, the overall Coulomb potential on the surface also decrease due to the consequential charge loss and thus results in lowering the KE of the protons with time. Our semi-classical and quantum dynamical simulations provide additional support to our findings, as elaborated in the later section on theoretical modeling.

#### Visualizing Surface Charge Dynamics

In Fig. 5.4, we observe that the proton momentum distributions in the low KE region exhibit angular broadening. Figure 5.4B presents the proton momentum angular distribution  $\Theta$ , defined as  $\Theta = \arctan(p_u/p_z)$ , as a function of the pump-probe time delays. To quantify the delay-dependent angular broadening, we fitted the angular distributions for each time delay to a typical Gaussian function with full-width-half-maximum (FWHM) denoted by  $\Delta\Theta$ . Fig. 5.4A shows the proton angular distribution induced by a single 2  $\mu$ m, which correlates with the initial local charge distribution induced by the pump-pulse. The FWHM value of this angular distribution is  $\Delta \Theta \sim 52.2^{\circ}$  and acts as a baseline for defining the onset of the broadening of the delay-dependent proton emission. The obtained  $\Delta\Theta$ values as a function of time delays are shown in Fig. 5.4C. The variation in  $\Delta\Theta$  allows for inspecting the dynamics of time-resolved surface charges during the redistribution process. In Fig. 5.4C, it can be observed that  $\Delta \Theta$  exhibits exponential broadening. The broadening is characterized by a faster rate of change at smaller delays (< 30 ps) that transitions to a slower rate of change at larger time delays  $(>100 \,\mathrm{ps})$ , eventually nearly approaching a plateau. It is obvious that as the delay increases, the angular distribution becomes broader, accompanied by a decreasing proton KE (see Fig. 5.4A). For instance, as the delay increases from ~ 4 ps to ~ 30 ps,  $\Delta\Theta$  broadens from ~ 55.2° to ~ 94.1° and the proton KE accordingly decreases from  $\sim 24 \text{ eV}$  to  $\sim 7.7 \text{ eV}$ .



Figure 5.4: (A) The angular distribution of protons for single 2 µm pulse (blue curve) fitted with a typical Gaussian curve (orange curve). The green-dashed line denotes the full-width at half-maximum (FWHM) of the Gaussian fit. (B) Normalized proton angular distributions  $\Theta$  as a function of positive time delay in the experiment. (C) Change in the angular distribution of protons as a function of time, quantified by the FWHM values extracted from the Gaussian fits for the time-sliced values. (D) Snapshots of the measured 3D proton momentum angular distribution at different time delays. The 3D proton momentum distribution ( $\phi$ ,  $\Theta$ , r) is radially integrated and then mapped onto a unit sphere, generating a two-dimensional density map ( $\phi$ ,  $\Theta$ ). This spherical projection involves coordinates defined by the elevation angle ( $\phi$ ) and azimuthal angle ( $\Theta$ ), each within specific intervals. Here,  $\Theta$  ranges from  $[-\pi, \pi]$ , relative to the x-axis (direction of propagation), while  $\phi$  spans  $[-\pi/2, \pi/2]$  concerning the y - z plane (pump polarization - TOF). The color scale visually represents the normalized count of protons captured within each solid angle.

Figure 5.5 shows that as the angle  $\Theta$  increases, indicating a broader angular distribution, the proton KE decreases significantly. This observed relationship strongly suggests that broader angular distributions of emitted protons are associated with lower overall proton KE. The observed delay-dependent broadening of the proton angular distribution and decrease of the proton KE clearly indicate the relaxation of the surface charge density on the nanoparticles after laser irradiation. It is attributed to the diminishing Coulomb force, which arises due to the reduced local surface charge density as the charge distribution spreads out. Since the directionality of proton emission closely correlates with the surface charge distribution, a broader angular distribution of protons is expected when the charge distribution itself becomes wider. Such redistribution scenario can be intuitively visualized from the snapshots of the measured proton final momentum distributions shown in Fig. 5.4D. This visualization highlights the critical role that local surface charges play in weakening surface molecular bonds and initiating dissociation with the arrival of a second pulse.



Figure 5.5: Proton KE decay as a function of  $\Theta$ .

#### 5.3.1 Laser polarization and intensity effects

The orthogonal selection of the polarization of pump and probe pulses was a crucial aspect of the present study. It allowed the tracking of the surface charge dynamics on individual nanoparticles as it leads to distinct optical and chemical hotspots on the nanoparticle surface pertaining to each pulse. Proton emission solely from the 2 µm or 1 µm pulses contrasts with the ion yield distributions resulting from the joint action of pump and probe pulses at variable delays. As discussed earlier, this distribution aligns with the polarization direction of the pump pulse and is orthogonal to the probe pulse when using orthogonally polarized pump and probe pulses. To verify the phenomena, proton emission from the joint action of pump-probe pulses having same polarization direction at variable time delays was also measured.

The measured KE spectrum of the protons as a function of pump-probe time delay polarized in the same direction (along y-axis) is shown in Fig. 5.6A. Fig. 5.6B-C depicts the time integrated proton momentum distribution for both, negative and positive delays. Fig. 5.6 is analogous to Fig. 5.2, except that both pump and probe pulses have the same polarization direction, contrasting with the latter scenario where the pump-probe pulses were orthogonally polarized to each other. In contrast to Figure 5.2B, which illustrates proton emission along the z-direction, corresponding to the polarization direction of the first arriving pulse (1 µm in this case), Figure 5.6B shows dipolar proton emission along the y-direction. This change aligns with the alteration in the polarization direction of the 1 µm pulse along the y-axis. It holds the interpretation that the first arriving pump pulse is primarily responsible for generating surface charges that lead to the weakening of surface molecular adsorbate bonds. The subsequent probe pulse, in turn, irrespective of it's polarization direction, facilitates bond rupture and drives molecular dissociation from the optical hotspots associated with the pump pulse. It is worth noting that this phenomenon is only observed in the time-dependent proton KE decay signal whereas the



Figure 5.6: (A) The proton KE spectrum was measured as a function of the time delay between 2 µm and 1 µm pulses. Both pulses share the same polarization direction, aligned along the y-axis. For positive delays, the 2 µm pulse precedes the 1 µm pulse, whereas for negative delays, the order is reversed. (B, C) The time-integrated proton momentum distributions in the  $p_x = 0$  plane. These distributions illustrate the delay-dependent energy decay signal for negative (Region 2) and positive (Region 3) delays, respectively.

time-independent individual contributions of the respective laser pulses still exhibits the dipolar emission along the respective laser polarization directions.

In our experiment, we also investigated the impact of varying the laser intensities of both pump and probe pulses on surface charge dynamics. This investigation is important for reinforcing the understanding of the reliance on surface charges in driving surface molecular dissociation through bond weakening. Additionally, it helps in distinguishing between the various processes occurring at the nanoscale across different timescales. The bar histogram in Fig. 5.7 encapsulates the variation of intensities on the ionization dynamics of the nanoparticle surface described in terms of ionization yields. Here, the total number of ionization events serves as an indicator for the relative strength of the laser pulse. This is based on the fact that in strong-field laser ionization experiments the total ionization events, that is the number of atoms or molecules that have been ionized by the laser pulse, tend to increase non-linearly with higher laser intensities [122]. In Fig. 5.7, the events ratio is defined as the total number of ionization events for 1 µm pulse divided by the same



Figure 5.7: Relative proton yield as a function of different pump-probe intensities. Here E1, E2 and E3 denotes the ratio of the total number of ionization events corresponding to the probe pulse  $(1 \ \mu m)$  divided by the events recorded with individual pump  $(2 \ \mu m)$  pulses for different laser intensities. The purple bars indicate the total yield of protons in the KE decay signal on the negative delay side and orange bars indicate the total proton yield on the positive delay side in the proton KE spectrum of different measurements with different laser intensities.

for  $2\,\mu\mathrm{m}$  pulse.

It is observed that the proton dissociation due to 1 µm laser pulse is much less than that observed with single 2 µm laser pulses. This effect is visible in the respective role of these pulses acting as the pump or the probe. Correspondingly, the purple bar is relative lower than the orange bar in Fig. 5.7 where the 2 µm pulse act as the pump and generates a greater number of surface charges, and therefore higher proton yield. On increasing the relative strengths between the pump and the probe pulses, it was noted that the parameters of the time-dependent bi-exponential fit of the proton KE decay remains the same but the relative yields of the time-dependent signal changes, as evident in Fig. 5.7. This suggests that as the relative laser strength of the pump-probe pulses increases, the number of protons in the time-dependent KE decay signal driven by each pulse also increases. This indicates that a higher number of surface charges leads to a greater effect on adjacent surface molecular groups, weakening bonds and consequently resulting in a higher frequency of proton dissociation events. This observation further emphasizes the role of laser-induced surface charges in inducing bond weakening, thereby distinguishing their influence from photo-thermal processes.

#### 5.3.2 Effect of surface charge redistribution on other fragments

In addition to the comprehensive examination of processes detailed till now, which predominantly revolved around monitoring proton behavior as an indicative marker of nanoparticle surface charge density, the objective of this section is to study more charged fragments emitted from the nanoparticle surface. The time-of-flight measurements not only served to record the presence of other fragments like  $H_2^+$ ,  $H_3^+$  fragments, but also allowed us to record the time-resolved emission dynamics of these fragments.

In a prior study, reaction nanoscopy highlighted the role of SiO<sub>2</sub> nanoparticles as catalysts in the formation of trihydrogen from water molecules residing on the nanoparticle surface through bi-molecular photo-reactions. In contrast, in the current experiment, the origin of  $H_2^+$  and  $H_3^+$  fragments lies in the -O-CH<sub>2</sub>CH<sub>3</sub> (O-ethoxy) groups attached to the surface. This stems from the use of ethanol as the solvent for nanoparticle dispersion resulting in physiosorbed surface molecules and the chemisorbed groups from using TEOS during the synthesis as detailed in the experimental methods in Chapter 3. While the formation of  $H_2^+$  and  $H_3^+$  fragments from organic molecules has been previously studied [123], the charged nanoparticle surface significantly enhances these reactions, resulting in higher yields with highly energetic fragments compared to earlier research.



Figure 5.8: (A) Measured KE spectrum of  $H_2^+$  ions as a function of time delay between  $2 \mu m$  and  $1 \mu m$  pulses. (B) Comparison between the KE decay for  $H^+$  and  $H_2^+$ . The data shown are the mean values of the KE spectrum filtered on the decay curve for both the species individually.

Figure 5.8 illustrates the recorded time-dependent KE spectrum of  $H_2^+$  ions. Notably, the KE decay pattern exhibited by  $H_2^+$  ions closely resembles that of protons. However, the  $H_2^+$  ions are observed to possess lower average kinetic energies comparatively. This disparity can be attributed to the energy expended during the formation of  $H_2^+$  ions along with the surface charge loss exhibited by the nanoparticle surface due to proton detachment. Furthermore, the differing masses of these fragments can exert an influence on their interactions with the charged nanoparticle surface. Upon examining the KE decay curve, we observe that the fast component of the bi-exponential fit yields a time constant of 25.3 ps for  $H_2^+$  ions. This suggests that  $H_2^+$  ions are emitted from the nanoparticle surface at a comparatively slower rate. The reason behind this reduced speed might lie in the lighter mass of  $H^+$  ions, which causes the protons to escape more rapidly in comparison to the  $H_2^+$ . Interestingly, the slower component of the decay curve remains consistent with the slower time constant ( $\tau_{slow}$ ) obtained for protons i.e.,  $\sim 70$  ps. This consistency signifies a shared underlying process that governs the slower charge dynamics.

#### 5.3.3 Size-dependent surface charge dynamics

The discussion thus far has focused on the generation and redistribution of surface charges. These processes can vary significantly with changes in the nanoparticle size due to the inherent size dependence in the laser-nanoparticle interaction, as described in the previous chapter utilizing the Mie parameter. Therefore, it becomes particularly intriguing to explore the particle size effect in the time-resolved study presented in this chapter, given its potential influence on all the processes discussed. Figures 5.9A-C illustrate the measured proton KE spectra as a function of the time delay between the pump and probe pulses for nanoparticles of sizes 200 nm, 300 nm, and 600 nm, respectively. A quick look at the 2D spectra reveals striking similarities between the temporal evolution of the KE spectra for particles of different sizes. To facilitate a more intuitive comparison, we extracted the mean value curve of the proton KE spectra obtained from the delay-dependent curves. Employing a bi-exponential fit to model the proton KE decay profiles of the mean value curves, we can extract the overall timescales of the different processes characterizing the spatial surface charge redistribution dynamics as a function of nanoparticle size. The biexponential fit revealed distinct values of the time constants for nanoparticles of different sizes which are displayed in Tab. 5.1.



Figure 5.9:  $(\mathbf{A}-\mathbf{B})$  Proton KE distributions as a function of the time delay measured for 200 nm  $(\mathbf{A})$ , 300 nm  $(\mathbf{B})$ , and 600 nm  $(\mathbf{C})$  diameter particles.

The differences in time constants and amplitudes between nanoparticles of different sizes offer insights into various noteworthy features. The "fast" time constants ( $\tau_{fast}$ ) increase slightly with nanoparticle size (( $\sim 8.8 \text{ ps}$  for 200 nm, ( $\sim 10.3 \text{ ps}$  for 300 nm, and ( $\sim 13.0 \text{ ps}$ for 600 nm). As the proton KE is determine by the electrostatic repulsion from the surface charges at any time, higher surface area in larger particles leads to slower overall charge redistribution due to longer diffusion distances. Smaller nanoparticles, with their smaller surface area, see a broader spreading of charge distribution at any given moment. This results in a wider surface distribution with a lower density, leading to a reduced proton final KE. The "slow" time constants ( $\tau_{slow}$ ) show minimal variation across sizes ((~63.4 ps, (~68.1 ps, and (~69.8 ps)). This suggests that the slower process, is less dependent on the particle size.

The consistently similar amplitude of the fast process  $(A_1)$  around (~20 for different sizes and the similar mean proton KE around zero time delayndicate that the locally induced surface charges by the pump exhibit comparable local charge densities. The ionization cross-section increases with an increase in particle size, resulting in a greater number of surface charges. However, this effect is balanced by the overall increase in the surface area, leading to comparable surface charge densities, as validated theoretically and discussed in the simulations section later. The amplitude of the slow process  $(A_2)$  increases steadily with size ( $\sim 5.3$  for 200 nm, ( $\sim 7$  for 300 nm, and ( $\sim 7.8$  for 600 nm). This suggests that the slow process becomes more dominant for larger particles, potentially contributing more significantly to the overall energy decay. This might occur due to increase in surface area with increase in nanoparticle size leading to longer diffusion lengths slowing down the fast decay. Overall, the surface charges on particles of varying sizes are observed to redistribute angularly towards an equilibrium isotropic distribution. Although the observed trends provide valuable insights, it is essential to employ theoretical modeling to conclusively establish their connection to specific mechanisms. Further elucidation on the underlying physical mechanisms is provided in the theory section of this chapter.

#### Field-propagation effect on surface charge dynamics

The size-dependent interaction and field-propagation effects of nanoparticles with wavelengths used in the current experiment for the pump and probe pulses at 2 µm and 1 µm were discussed in detail in the previous chapter. In the current time-resolved study, field propagation effects were also observed. Figure 5.10A offers a glimpse of the delaydependent proton angular distribution ( $\theta_{xy}$ ) recorded for 600 nm nanoparticles in the polarization-propagation ( $p_z = 0$ ) plane. It is calculated as  $\theta_{xy} = \arctan(p_y/p_x)$ . In addition to the observed angular broadening, a delay-dependent outward deflection in the mean emission angle  $\theta_{xy}^{mean}$  is observed as shown in Fig. 5.10A on top of the 2D spectrum with the white dots. Considering the field propagation effects in nanoparticles and the generation of surface charges due to strong-field ionization at the rear side of the 600 nm

Particle Size	$A_1$	$A_2$	$\tau_{\rm fast} \ (ps)$	$\tau_{\rm slow} \ (ps)$
200 nm	20	5.3	$8.8 \pm 0.2$	$65.02 \pm 3.2$
300 nm	20	7	$10.3 \pm 0.1$	$70.1 \pm 1.8$
600 nm	20	7.8	$15.0 \pm 0.4$	$80.02 \pm 2.5$

Table 5.1: Bi-exponential fit parameters for nanoparticles of different sizes

spherical silica nanoparticles [59, 93], we observe that subsequent charge redistribution is also more dominant on the rear side of the nanoparticle. This asymmetry aligns with the laser propagation direction, following the initial asymmetric charge generation process.



Figure 5.10: (A) Normalized proton angular distribution  $\theta_{xy}$  (laser-polarizationpropagation plane) as a function of the time delay, as measured for 600 nm particles. The white-solid circles show the time-sliced mean values. (B) Extracted time-sliced mean values as a function of time delay measured for 200 nm, 300 nm, and 600 nm particles as indicated.

This is evident from Fig. 5.10B, where we extracted the  $\theta_{xy}^{mean}$  values for the upper hemisphere with respect to the laser polarization direction as a function of time delay, encompassing particles of different sizes. The field-induced deflection of  $\theta_{xy}^{mean}$  is notably more pronounced for 600 nm particles compared to 300 nm particles, particularly evident at shorter delays. This discrepancy is attributed to variations in the locations of maximum near-field enhancement hotspots and, consequently, differences in surface charge density between the two sizes. Around zero time delay, the maximum emission yield is centered around the poles at 90° for 300 nm nanoparticles. In contrast, for 600 nm nanoparticles, the localization shifts to the rear side of the nanoparticle surface along the laser propagation direction, with the deflection beginning around ~75°. With increasing delay,  $\theta_{xy}^{mean}$ continues to deflect towards the poles along the laser polarization direction ( $\pm 90^{\circ}$ ) until it reaches a plateau, indicating that the charge distributions in the upper and lower hemispheres converge, suggesting an isotropic distribution across the nanoparticle surface. For 300 nm particles, this plateau is reached earlier (around 40 ps) than for 600 nm particles (approximately 60 ps) due to the weaker field-propagation effect and smaller surface area, influencing charge diffusion. As for 200 nm particles, the field-propagation effect is notably weaker, and any observed  $\theta_{xy}^{mean}$  deflection is marginal within the experimental error bars.



Figure 5.11: (A,B) Modeled point-charge-sampling of positive surface charges (red dots) and protons (blue dots) on a d=300 nm SiO<sub>2</sub> nanosphere at a time of 0 ps (A) and 100 ps (B), respectively. Each point charges on the sphere is defined by the inclination angle  $\Theta$  and the azimuthal angle  $\Phi$ , in the intervals [0;  $\pi$ ] and [- $\pi$ ;  $\pi$ ], respectively.

# 5.4 Theoretical Modeling and Results

#### 5.4.1 d-CTMC Simulations

To understand how charges redistribute on the surface of  $SiO_2$  nanoparticles, we employed d-CTMC simulations. The d-CTMC model simulates two key phases of ionization of  $SiO_2$  nanospheres with femtosecond laser pulses: the initial ionization phase generating the surface charges and the subsequent, post-laser surface charge relaxation phase.

The ionization phase is centered around creating a localized positive charge distribution on a spherical nanoparticle of a defined size, here taken as a 300 nm SiO<sub>2</sub> nanosphere. The positive charges arise from the release of electrons through tunneling ionization utilizing the ADK ionization rate. This ionization process occurs due to the enhanced electric fields generated through the laser-nanoparticle interaction. For proton generation, we sampled proton birth positions for the first laser pulse based on dissociation ionization probabilities following the power-law dependence, I<sup>n</sup>. The value of n is chosen as 26 for the current study adapted for the 2 µm wavelength in alignment with methods used in previous studies on reaction nanoscopy [52, 63]. Additionally, we incorporated a radial Gaussian distribution ( $r_0 = 150$  nm,  $\sigma_r = 30$  nm) to account for the spatial distribution of molecules as elaborated in Chapter 2. The number of sampled static surface charges for the normalization of initial charge distribution were estimated around 1600e, determined by fitting the proton KE distribution induced by a single 2 µm laser pulse at an intensity of  $1.8 \times 10^{13}$  W/cm<sup>2</sup>.

Following the laser pulse, the nanoparticle surface remains highly positively charged,



Figure 5.12: (A) Simulated initial angular distribution of surface charges and (B) proton birth positions at t = 0 ps, respectively, on a d = 300 nm SiO<sub>2</sub> nanosphere in the  $\Theta - \Phi$ plane. (C, D) Simulated and experimental proton momentum distribution at time, t = 0 ps, respectively, projected in the  $\Theta - \Phi$  plane similar to (B, C). (E) The  $\Delta\Theta$  values, dependent on the delay, represent the full width at half maximum of the angular distribution ( $\Theta$ ). These values were obtained through Gaussian fittings applied to the time-sliced  $\Theta$  distributions. The gray shaded area represents the standard errors derived from these fittings. Additionally, the plot illustrates the angular broadening observed in simulated angular distributions: surface charges (depicted by the orange dashed curve), proton birth positions (illustrated by the yellow dashed-dot curve), and proton momentum distributions (shown by the pink solid curve). The 2D color plots represent normalized counts ranging from 0 to 1.

while entering the post-laser charge relaxation phase. During this phase, the diffusion of the surface charges and charge loss become the dominant processes. The model incorporates a time-dependent diffusion coefficient for the 3D random walk representing charge diffusion, with each step size following a Gaussian distribution. To optimize computational efficiency while maintaining result accuracy, a 1 ps time step is chosen. At each time step, protons undergo classical propagation influenced by the electric field induced by the corresponding surface charge distribution, and their 3D momentum spectra are collected. Finally, the diffusion coefficient and charge decay constant are adjusted as fitting parameters to match the model's output with experimental observations.

Our model assumes that proton generation is directly affected by surface charge distribution. Specifically, the presence of surface charge influences the bonding of nearby molecules, leading to their weakening. To account for this influence and the non-uniform distribution of both charge density and potential proton generation sites, we employed an initial sampling region for protons following the power-law dependence as discussed earlier. The initially sampled proton birth positions are then diffused around the nanoparticle surface following the distribution of surface charges. Furthermore, the simulations incorporate a second pulse to trigger proton dissociation considering a unit probability of ionization in the regions of high surface charge density. This pulse likely induces bond stretching through the electric field it generates, ultimately triggering the dissociation of already weakened bonds. Consequently, proton birth positions follow the surface charge distribution.

Figure 5.11A illustrates the initial distributions of surface charges and proton birth positions, respectively, at the start of the diffusion process (i.e., t = 0 ps). Figure 5.11B shows the positions of surface charges and corresponding proton birth positions at  $t = 100 \, \text{ps}$ , after achieving a nearly isotropic distribution through diffusion. To gain further insight, we plotted the two-dimensional density maps of the surface charge and proton birth position distributions projected onto the  $\Theta$ - $\Phi$  plane as shown in 5.12A-B. Here,  $\Theta$  and  $\Phi$  are defined as illustrated in Fig. 5.4D. Due to mirror symmetry with respect to the x-z plane, the  $\Theta$ values are only displayed from 0 to  $\pi$ . Figure 5.12C depicts the corresponding simulated proton momentum distribution while Fig. 5.12D provides a comparison to the measured proton momentum distribution obtained using 2 µm laser pulses. The subsequent temporal variation of the  $\Delta\Theta$  values, derived from the FWHM values of Gaussian fits applied to time-sliced data implementing the same procedure as followed previously (see Fig. 5.4A-C), for the different distributions is collectively presented in Fig. 5.12E. Our results reveal an exponential redistribution of surface charges, accompanied by a broader distribution of proton birth positions and simulated proton momentum distribution consistent with the experimentally measured data. Importantly, our analysis serves a dual purpose: it not only elucidates the connection between the initial proton positions (Fig. 5.12B) and their subsequent momentum distribution (see Fig. 5.12C, D) but also underscores the impact of surface charge distribution on proton emission (Fig. 5.12A). These observations unequivocally demonstrate the influence of surface charge redistribution on both, the protons birth positions and the distribution of their final momentum. This extends the near one-to-one mapping between proton momentum distribution and proton emission in real space [93] to the underlying surface charge distribution.

By converting the proton emission angle width into the spatial position of surface charges using the formula:

$$S_R(\Theta) = \pi \left(\frac{\Delta\Theta(t) - \Delta\Theta(t=0)}{2 \times 360^\circ}\right) d, \tag{5.2}$$

where d represents the diameter of the nanoparticle, we can track the time-dependent relative change in surface charge locations compared to their initial birth positions on the nanoparticle surfaces. In Fig. 5.11E, the right-purple axis represents the relative change in proton birth positions  $(S_R)$ , spatially on a 300 nm SiO<sub>2</sub> nanosphere. This calculation relies on the nearly one-to-one mapping between the initial proton birth position and the final proton momentum [93]. The relative spatial movement of surface charges is traced through the dissociation of protons induced by the presence of these surface charges. Based on the obtained simulation results, we observe a change of  $\Delta \Theta \approx 40^{\circ}$  in the width of the angular distribution of surface charges across the 300 nm SiO<sub>2</sub> nanoparticle. This translates to a change of  $\sim 52$  nm in the spatial displacement of the surface charges. Interestingly, the initial distribution of proton birth positions is much narrower. However, it follows the trend of the surface charge distribution, gradually broadening until it resembles a near-isotropic pattern, mirroring the final state of the surface charges. This results in a significant shift of around  $\sim 105$  nm in the center of the distribution of proton birth positions. However, it's worth noting that the actual distances covered by the charges may vary naturally because of the stochastic nature of charge positions and their movement directions. Nonetheless, our method allows us to precisely observe the spatiotemporal evolution of surface charge density with nanoscopic spatial resolution and femtosecond-temporal precision. To this end, we have visualized in 4D the surface charge redistribution dynamics on subwavelength-sized and isolated nanoparticles at the nanoscale.



Figure 5.13: Mean proton KE values filtered on the KE decay signal obtained from simulations using various parameter sets as a function of time, alongside experimental values. The dashed curve represents the decay of proton KE over time due to surface charge diffusion, marked by a dash-dotted line. The solid line combines both surface charge diffusion and charge loss scenarios. Purple dots, accompanied by gray error bars, represent experimentally measured mean proton KE values along with their associated standard deviations.

After laser-induced ionization, the initially localized surface charge undergoes relaxation leading to a decrease in local charge density as the charge distribution starts diffusing across the nanoparticle surface. Initially, we attributed the KE decay observed in the experimental data solely to the decrease in local charge density through diffusion. However, comparing experimental data with diffusion-only simulations exposed a significant discrepancy, cf. Fig. 5.13. Diffusion alone couldn't account for the substantial KE decrease. The introduction of surface charge loss as an additional mechanism provides a more comprehensive explanation. One potential cause of this loss could be the proton detachment process itself. As protons are emitted, they carry away some charge, altering the overall surface charge distribution. This change significantly influences the Coulomb force experienced by subsequent protons, impacting their acceleration and ultimately their KE. The charge loss mechanism effectively bridges the gap between theory and experiment. To model the charge loss process, we employed an exponential decay function analogous to the established charge decay phenomenon as described in Chapter 2. We examined the individual and combined effect of both processes—diffusion and charge loss— in surface charge redistribution and their influence in determining the proton emission dynamics. Figure 5.13 depicts the impact of the individual and combined effects of diffusion and charge loss on proton KE. It is observed that while diffusion plays a role in KE decay, surface charge loss emerges as a crucial factor in explaining the observed behavior.

The d-CTMC simulation results, while primarily qualitative, successfully capture significant trends observed in the experimental data, such as the decay in proton KE and the broadening of the proton angular momentum distribution, as depicted in Figures 5.12B and 5.11E, respectively. These results also consider how proton dynamics are influenced under varying physical processes. From the simulations, we extracted two key parameters: a diffusion coefficient of approximately  $1.35 \text{ cm}^2/\text{s}$ , which quantifies the rate of charge diffusion across the nanoparticle surface, and a charge decay constant of roughly 40 ns, reflecting the timescale for charge loss and the presence of a residual charge component. To validate these theoretical constants, we extended the simulations to check the nanoparticle size dependence. The results, represented by red-dashed curves in Figures 5.9A-C, closely match experimental data, validating the values of the extracted diffusion and charge loss constants. This observation emphasizes that the obtained constants are not influenced by the size of the nanoparticles, but rather depend solely on the material itself (SiO<sub>2</sub> in our case). Additionally, the analysis reinforced the understanding that smaller nanoparticles exhibit faster charge redistribution dynamics compared to larger ones, highlighting the particle size influence on these dynamics. In conclusion, the close alignment between theory and experiment allowed for a comprehensive and quantitative dissection of the distinct mechanisms and the associated timescales of the processes governing surface charge redistribution.

#### 5.4.2 NAQMD Simulations

To investigate the influence of surface charge on bond softening and subsequent proton dissociation in amorphous silica nanoparticles, NAQMD simulations [124, 125] were performed by Thomas M. Linker, at Stanford University.

The NAQMD simulations were conducted on an amorphous silica surface terminated with Si-OH and Si-OH<sub>2</sub> groups, with the presence of excited holes from the valence band maximum (VBM). A multi-scale approach was employed due to the incapability of first principle simulations to handle surfaces on the size of the nanoparticle. A strong DC field was applied along the silica surface to mimic the effect of the global field generated by the total ionized charge density on the nanosphere surface. This is similar to globally informed Hartree potential frameworks in divide-and-conquer density functional theory [125]. Consequently, the simulated silica surface represented approximately a  $\sim 1 \text{ nm}^2$  segment embedded within an ionized nanosphere.

Estimating the induced fields on the nanosphere resulting from the non-uniform ionized



Figure 5.14: (A) A simulated silica slab representing a roughly 1 nm<sup>2</sup> section of silica under the influence of a strong DC field generated by surface charges. The white lines represent the applied periodic boundary conditions. (B) Dynamics of O-H bonds, comparing situations with and without the presence of holes, courtesy of Thomas M. Linker.

charge density was the initial step. The Lumerical FDTD solver was utilized to determine the near field enhancement at the nanosphere surface for given pump pulse. Subsequently, an ionized charge distribution was generated from the local optical fields using Ammosov, Delone, and Krainov (ADK) theory[79]. The integrated ADK rate was employed to ascertain the probability density of ionization for any given surface area element, with the total ionized charge density then set as the density of "SiO<sub>2</sub>" in crystalline silica times the ionization probability [51]. For instance, the charge distribution at the surface as a function of the polar angle  $\Theta$  for a 50 nm particle in which approximately 12,000 electrons were ionized using an intensity of  $5 \times 10^{13}$  W/cm<sup>2</sup> is depicted in Fig. 5.15A. The electric field induced by the charge density was obtained by solving Poisson's equation via multipole expansion, and the resulting field at the nanoparticle surface is displayed in Fig. 5.15B. Despite several approximations involved in obtaining this field, the primary objective was to establish boundary conditions for Non-Adiabatic Quantum Molecular Dynamics (NAQMD) simulations. These simulations only required an order of magnitude estimate of the expected electric fields generated during experiments.

Figure 5.14A portrays the replicated simulation slab, with a white box denoting the periodic boundary condition. NAQMD simulations were performed on a 14.32 Å cubic amorphous silica structure. A hydrogen-terminated surface was created along one of the cubic axes, and additional vacuum was added to prevent image interactions. An electric field of approximately 0.02 atomic units (equivalent to  $\sim 1 \text{ V/Å}$ ) was applied using a sawtooth potential. NAQMD simulations, an ab-initio molecular dynamics approach, were utilized to integrate the trajectories of all atoms by computing their intermolecular



Figure 5.15: (A) Distribution of charges on the surface with respect to the polar angle  $\theta$  at the nanosphere. (B) Computed electric field at the nanoparticle surface derived from the charge density obtained using Poisson's equation through a multipole expansion. (C) Evolution of an O-H bond on the surface, emphasizing the hole wave-functions exhibiting the highest Mulliken population. (D) Reduction in vibrational energy linked to the O-H stretching mode, observed in the Fourier transform of the dynamics of O-H bond length, courtesy of Thomas M. Linker.

forces from first principles within the framework of density functional theory (DFT). The Perdew-Burke-Ernzerhof (PBE) version of generalized gradient approximation (GGA) was employed to approximate the exchange-correlation functional in the DFT approach [126]. Van der Waals corrections were incorporated using the DFT-D scheme [127]. The projected augmented wave (PAW) method was employed to calculate electronic states within a plane wave basis set, with projector functions generated for the Si-3s and 3p states, O-2s and 2p states, and the 1s state for hydrogen. A plane wave cutoff energy of 35 Ry was selected. NAQMD allowed for the modeling of the dynamics of excited carriers within the framework of time-dependent DFT, with excited state transitions modeled using the fewest switch surface hopping method [128]. The simulations were conducted in the microcanonical ensemble at 300 K, employing the NAQMD algorithm implemented in the QXMD quantum molecular dynamics simulation code [129]. Further details of the NAQMD algorithm are provided in references [129, 124, 125].

#### Investigation of O-H Bond Dynamics

Our primary focus was on the dynamics of the O-H bond on the silica surface exhibiting the highest Mulliken population hole wavefunction. By examining the bond length evolution with and without the presence of excited holes, we were able to elucidate the impact of charge generation on bond stability. Fig. 5.14B illustrates the bond dynamics for the O-H bond with and without the presence of any holes.

The simulations revealed that excitation of two holes from the valence band maximum (VBM) resulted in rapid dissociation of the O-H bond. In contrast, excitation of a single hole led to a significant softening of the bond, characterized by an increased stretching length and lower stretching frequency compared to the field and hole-free ground state, as shown in Fig. 5.15C. This softening effect is further visualized by the decline in O-H stretching vibrational energy observed in the Fourier transform of the bond length dynamics shown in Fig. 5.15D, which may lead to breaking during the stretching of the bond by the probe pulse. The initial pump pulse is expected to generate numerous holes, which can quickly disassociate O-H bonds and depart from the nanoparticle. Remaining holes that have not led to dissociation still soften the O-H bond, potentially leading to later bond breaking during the stretching induced by the probe pulse field. As the local/neighboring number of surface charges is anticipated to decrease over time due to proton detachment and diffusion, protons emitted by this dissociation pathway are expected to possess reduced KE over a delay time. In summary, our analysis reveals, on one hand, how surface charge redistribution dynamics impact proton birth positions and their ultimate momentum as shown using d-CTMC simulations, and on the other hand, underscores the critical role of surface charge distribution in proton emission via surface bond weakening as demonstrated using NAQMD simulations.

### 5.5 Discussion

Our d-CTMC simulations reveal that the angular broadening observed in the proton momentum distribution primarily arises from diffusion, which disperses initially localized surface charges over time. However, simulations focusing solely on diffusion fail to accurately replicate the entire decay profile of proton KE, despite capturing the initial rapid decline. Incorporating charge loss due to proton detachment significantly enhances agreement with experimental data. Protons emitted through this mechanism experience reduced final KE due to weakened Coulomb forces stemming from lower charge density and increased charge separation on the nanoparticle surface. Analyzing proton energy loss enables us to investigate both local and overall surface charge density. Importantly, our study not only comprehends the roles of diffusion and charge loss in surface charge dynamics but also distinguishes them based on their characteristic timescales. Extracting and discerning these timescales on isolated nanoparticles allows for comparison with theoretical predictions, advancing our understanding of nanoparticle-driven catalysis and related charge-mediated processes. The calculated diffusion coefficient of approximately  $1.35 \text{ cm}^2/\text{s}$  from the simulations reveals unique characteristics resulting from the strong-field ionization of SiO<sub>2</sub> nanoparticles. Although this value might seem small when compared to a degenerate electron gas (such as a simple metal) [130], it is surprisingly large relative to typically reported photocarrier transport coefficients [131, 132, 133]. Furthermore, compared to the bulk diffusion constant of a typical photocatalytic material TiO<sub>2</sub>, our reported diffusion constant is approximately three orders of magnitude larger [134]. The corresponding charge carrier mobility associated with our reported diffusion constant falls on the high end of what is observed in heavily doped wide bandgap semiconductors [135]. This intriguing behavior can be attributed to the trapping field generated by the positively charged surface and the presence of free electrons resulting from strong field ionization of SiO<sub>2</sub> nanoparticles, leading to robust charge interactions and increased charge mobility at the nanoparticle surface [55]. Consequently, our reported diffusion constant, lying between that of a heavily doped semiconductor and a degenerate electron gas, aligns consistently with this scenario.

Additionally, the charge decay constant, approximately 40 ns, exhibits similarities with reported values observed in analogous systems. For instance, in rutile  $\text{TiO}_2$ , the lifetimes of holes were found to exceed several hundred picoseconds (ps) [136]. This consistency underscores the relevance of our findings and their applicability to related materials. The development of next-generation photocatalytic materials heavily relies on our ability to understand and engineer charge carrier lifetime and diffusion properties. Typically, longer charge migration times are sought to maximize reactivity [137]. Our implemented pumpprobe reaction nanoscopy technique allows us to evaluate these properties at the nanoscale, providing valuable insights for designing efficient materials.

While our theoretical framework offers a clear and intuitive interpretation of the experimental observations, we acknowledge limitations due to simplifying assumptions. Factors like charge-charge interactions and surface scattering, which influence diffusion and charge loss dynamics, are not explicitly considered. Incorporating these complexities would lead to a more quantitative and comprehensive understanding of nanoscale processes. Despite these limitations, our framework, combined with experimental findings, is able to provide valuable understanding of the fundamental processes governing surface charge redistribution on individual nanoparticles. This approach can serve as a foundation for comprehending diverse nanomaterials and broader charge-mediated phenomena occurring on nano-surfaces.

# 5.6 Conclusion

In conclusion, our study demonstrates the 4D visualization of surface charge dynamics on laser-irradiated dielectric silica nanoparticles using pump-probe reaction nanoscopy. Employing the reaction nanoscope, the projection of emitted positively charged ion fragments, such as protons, resulting from charge-assisted surface molecular dissociation at variable time delays, not only reveals the effect of surface charge on surface molecular bonding but also permits the spatiotemporal resolution of surface charge dynamics. Our semi-classical
#### 5.6 Conclusion

simulations reveal distinct timescales for the two key processes at play: diffusion and charge loss. This separation captures the observed bi-exponential decline in the KE of dissociated protons, providing a comprehensive understanding of surface charge behavior. Further exploration of the influence of surface charges, through NAQMD simulations, unveils their significant impact on the bonding of surface functional groups. This finding highlights the remarkable ability of charged nanoparticles to initiate and potentially control chemical reactions at their surfaces. Our technique to probe the local surface charge density in realtime, offers a powerful means to reconstruct both charge diffusion and decay constants, providing direct insight into the dynamic processes governed by them.

Beyond fundamental understanding, our results have intriguing implications for the catalytic reactivity of silica nanoparticles observed in previous studies [53]. By elucidating the intricate interplay between surface charge dynamics and reactivity, we can begin to explain and potentially predict the catalytic behavior of these materials. Expanding our understanding of surface charge dynamics on dielectric nanoparticles is set to produce invaluable insights into how the introduction of surface-bound charges can fine-tune catalytic activity. Importantly, our time-resolved single-nanoparticle experiments pave the way to a broader understanding of how the material composition and morphology of diverse nanoparticles influence charge carrier dynamics. This knowledge is critical for optimizing and designing next-generation materials with tailored charge-driven functionalities, ultimately leading to advancements in fields like heterogeneous catalysis.

## Chapter 6

# Trihydrogen cation formation on strong field-ionized gold nanoparticles

All the prior studies with reaction nanoscopy were limited to the use of dielectric nanoparticles owing to their versatility in handling, availability, and size tunability. In this chapter, we extend the applicability of reaction nanoscopy to metallic gold nanoparticles (AuNPs). The AuNPs are largely known for their remarkable catalytic properties, biocompatibility, and potential for functionalization [138]. The focus of the chapter will be to discuss the formation of the trihydogen cation on strong-field ionized AuNPs and difference in ionization yields obtained from citrate-capped spherical and polyhedral AuNPs. This follows a discussion on the factors contributing to the observed differences in yields. The chapter elucidates how variations in shape can alter the reaction landscape of the nanoparticle surface. This, in turn, provides insights into the catalytic properties of the nanoparticles and their varying behavior when interacting with strong laser fields.

### 6.1 Introduction

In recent years, AuNPs have emerged as key elements across a wide array of application domains, spanning biomedical applications [139], sensors [100], photonics [140], and catalysis [73]. These nanoparticles exemplify the transformative potential of nanoscale interactions, where surface properties govern unique phenomena and reactivity distinct from bulk behavior [2]. Specifically, the surface morphology of AuNPs significantly influences their reactivity, binding affinity, and stability [141], thereby impacting their performance in catalytic reactions, surface-enhanced spectroscopy [142], and therapeutic interventions [143]. Their high surface area-to-volume ratio not only enhances reactivity but also contributes to improved optical properties [9] and mechanical behaviors [144]. AuNPs exhibit exceptional interactions with light, primarily driven by their plasmonic properties [7]. When subjected to light irradiation, these interactions lead to a significant enhancement of the

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local electromagnetic field surrounding the nanoparticles [6].

Under the influence of strong laser fields, the near-field enhancement around the nanoparticle surface leads to ionization of the nanoparticle surface, creating localized surface charges with the ejection of electrons. Strong-field ionization of AuNPs under intense femtosecond laser pulses has been extensively investigated in recent years, shedding light on fundamental interactions governing nanoparticle behavior under extreme conditions. For instance, Powell et al. [145] investigated the manipulation of plasmonic properties in coreshell nanoparticles, showcasing the use of strong-field femtosecond laser pulses in achieving precise control of the optical response through non-linear light-matter interactions. Their work with  $Au/SiO_2$  nanoshells highlights the potential for exploiting the non-linear index of refraction of AuNPs under strong field ionization conditions. This manipulation was observed by analyzing photoelectrons emitted during the interaction, acting as a sensitive, sub-wavelength probe. Further insights into strong-field ionization dynamics of spherical AuNPs of different sizes have been provided by Saydanzad et al. [81], emphasizing the significance of residual charges alongside factors like photoelectron correlation and plasmonic near-fields in determining the energy and trajectory of emitted electrons. Unlike gaseous atoms, the ionized nanoparticle surfaces exhibit an intricate interplay between ejected photoelectrons and residual charges. The charge environment around the nanoparticle surface can affect the reactivity and catalytic properties of nanoparticles through mechanisms such as enhancing reactant adsorption, facilitating electron transfer processes, and modulating surface chemistry [24, 25]. Photoelectron spectroscopy has been instrumental in elucidating the mechanisms of nanoparticle ionization, including the interplay between enhanced near-fields, surface rescattering of electrons, and the generation of localized surface charges - a fundamental process underlying electron dynamics. Despite this significant impact, the influence of localized surface charges on the reactivity of AuNPs remains largely unexplored in current research.

The size and shape of nanoparticles exert significant control over the near-field distribution generated by strong-field laser pulses. This modulation of the near-field strength and spatial distribution consequently influences the localization of charges on the nanoparticle surface. Examining strong-field ionization in faceted and spherical AuNPs presents a valuable means for exploring this structure-dependent control. By investigating how variations in nanoparticle size, shape, and surface morphology influence the ionization process and subsequent charge distributions, we can elucidate fundamental processes underlying nanoparticle reactivity and catalytic performance. Numerous studies have been conducted to understand how surface features can influence the reactivity of nanoparticles [146, 147, 148]. However, the experimental methods used in such studies involve depositing the nanoparticles in a liquid state or onto a substrate for analysis. Both of these approaches can introduce interference, altering the properties of the nano-systems, and resulting in changes in their morphology, surface energy, or electronic structure [149, 150]. Moreover, substrates can introduce additional surface interactions that are absent at the single nanoparticle level, potentially masking or exaggerating certain catalytic features.

This study addresses such challenges in characterizing the interplay between nanoparticle morphology and reactivity at a single nanoparticle level using reaction nanoscopy [52]. As detailed in Chapter 2, reaction nanoscopy enables the investigation of energy and momentum distributions of ion fragments dissociated from nanoparticle surfaces during laser-induced reactions. It provides visualization and analysis of surface reactions with exceptional nanometric spatial resolution [93]. Here, we compare the dissociative photoionization yields from the surface of citrate-capped spherical and faceted AuNPs. The yield and spatial distributions of emitted fragments can vary based on the birth locations of the molecules on the vertices, edges, and faces of the nanoparticles and can be used as a probe of the local environment on the nanoparticle surface. We show how different shapes and sizes can alter the reaction landscape of the nanoparticle surface giving us insights into their reactivities and different behavior in their interaction with strong laser fields. This is achieved by focusing the attention on the formation of the trihydrogen cation on strong-field ionized AuNPs.

Trihydrogen cation ( $H_3^+$ ), also known as protonated molecular hydrogen, plays a crucial role in interstellar chemistry. As the simplest and most abundant triatomic ion in interstellar space,  $H_3^+$  plays a pivotal role in driving a multitude of chemical reactions. These reactions contribute to the formation of dense molecular clouds containing a large number of organic molecules [151, 152]. Multiple experimental approaches have been employed to understand the formation of  $H_3^+$  from various organic compounds. These investigations have employed a diverse set of methodologies such as electron impact [153], highly charged ion collisions [154], and intense laser fields [155, 156]. The chemical process involved in these studies features a two-step process. In the initial step, a doubly charged precursor ion undergoes fragmentation, yielding a neutral  $H_2$  molecule and a doubly charged fragment of the original organic molecule. The subsequent step involves the roaming hydrogen molecule abstracting a proton from the doubly charged fragment, ultimately resulting in the formation of an  $H_3^+$  ion.

# 6.2 Impact of surface features on gold nanoparticle reactivity

The experiment was conducted in the reaction nanoscope using laser pulses centered around the wavelength of 1 µm with pulse duration of  $\sim 35$  fs for the ionization of the AuNPs. The details of the experimental setup and the AuNPs used for the experiments are provided in Chapter 3. The graphical representation of the experimental scenario is depicted in Fig. 6.1. The specific morphology of AuNPs — whether faceted or spherical — crucially influences their interaction with strong laser fields. This variation significantly affects the generation and localization of surface charges, ultimately impacting nanoparticle reactivity. Faceted AuNPs feature well-defined, flat surfaces with sharp edges and corners. The electric field enhancement of the incident laser pulses is most pronounced at edges and corners, leading to highly localized regions of intense electric fields. Consequently, electron removal during strong-field ionization becomes more efficient at these hot spots, resulting in highly concentrated surface charge densities compared to spherical AuNPs. In contrast,



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Figure 6.1: Graphical representation emphasizing the impact of morphology on near-field enhancement, electron emission, and surface charge localization comparing spherical and faceted AuNPs. (i)-(ii) Scanning electron microscopy (SEM) images of spherical and faceted AuNPs, respectively, provided by Chenghao Fan.

the smooth, curved surfaces in spherical AuNPs experience a more uniform distribution of the electric fields, leading to a less intense and more evenly distributed localized charge density compared to their faceted counterparts. These variations in local charge density could profoundly impact the reactivity of different surface features on the AuNPs. Faceted particles with highly localized charges at edges and corners are expected to exhibit enhanced reactivity compared to spherical particles with more uniform charge distributions. This differential reactivity could potentially lead to the formation of specific reaction products, such as  $H_3^+$  cations, with higher yields at the hot spots of faceted AuNPs.

## 6.3 Nanoparticle shape-dependent variation in surface yields

Previous studies involving water/ethanol-covered silica  $(SiO_2)$  nanoparticles using reaction nanoscopy have consistently demonstrated a dominant presence of protons originating from the fragmentation of surface molecules upon laser interaction [52, 63, 46]. The momentum distribution of these protons exhibited a characteristic dipolar pattern aligned with the laser polarization, attributed to the sensitivity of ion emission to laser-induced nearfields [52, 46, 93]. Here, we present the first observations of similar dipolar emission in the proton momentum distribution obtained from the strong-field ionization of spherical, citrate-capped AuNPs, depicted in Fig. 6.2A. This finding expands the ability of reaction nanoscopy, demonstrating a nearly one-to-one mapping between proton emission in real space and their final observed momentum distribution for metallic AuNPs, extending the material systems beyond previously studied dielectric  $SiO_2$  nanoparticles. These observations represent noteworthy experimental evidence suggesting remarkable similarities in the underlying processes governing surface ion emission from the fragmentation of adsorbate molecules between metallic and dielectric nanoparticles under strong laser fields. In addition to the well-established dipolar emission observed with spherical nanoparticles, faceted AuNPs exhibit an additional feature in their proton momentum distribution, as shown in Fig. 6.2B. The spectrum reveals a low-momentum ring alongside the high-momentum dipolar structure, attributed to distinct surface features of faceted nanoparticles causing variations in ion emission behavior across different surface regions. Note that the momentum spectra for faceted particles represent an average over different particle orientations relative to the laser polarization direction.



Figure 6.2: (A)-(B) Measured proton momentum distribution for 100 nm spherical and faceted AuNPs, respectively.

The fragmentation of surface-bound citrate molecules upon laser irradiation is found to exhibit a strong dependence on the underlying nanoparticle structure. In the present study, we focus on the yields of  $H_3^+$  ions, a species rarely encountered in its free state due to its high reactivity. Figure 6.3A compares the time-of-flight (TOF) spectra of  $H_3^+$  ions emitted from 100 nm spherical and faceted AuNPs, alongside  $H_3^+$  ions emitted from 100 nm silica nanoparticles. Figure 6.3B depicts the measured momentum distribution of  $H_3^+$  ions



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Figure 6.3: (A) Measured time-of-flight (TOF) spectrum of selected ions emitted from 100 nm spherical AuNPs, faceted AuNPs and spherical silica nanoparticles (B) Measured  $H_3^+$  ion momentum distribution for 100 nm faceted AuNPs.

emitted from faceted AuNPs along the laser polarization direction. The distribution exhibits a weaker dipolar signature and low ion-momentum. In contrast to the adsorbed citrate molecules on the AuNPs, the observed fragments from SiO<sub>2</sub> nanoparticles originate from the surface-bound ethoxy  $(-O-CH_2CH_3)$  groups in addition to the silanols. The surface composition of  $SiO_2$  nanoparticles is detailed in another reference [46]. Our study demonstrates a significantly higher yield of  $H_3^+$  ions from citrate-capped AuNPs compared to silanol/ethoxy-covered  $SiO_2$  nanoparticles. This finding expands upon prior research on water-covered SiO<sub>2</sub> nanoparticles, elucidating the influence of organic citrate-molecules adsorbed onto nanoparticle surfaces on  $H_3^+$  ion yields. This allows for a direct comparison of how nanoparticle composition affects  $H_3^+$  ion yields and extends beyond the well-established production of  $H_3^+$  from other organic molecules in gaseous environments [123]. In addition, the yield of  $H_3^+$  ions is significantly increased for faceted AuNPs when compared to spherical counterparts. These findings emphasize two key points: firstly, metallic surfaces (AuNPs) show a higher tendency for  $H_3^+$  formation compared to dielectric surfaces (SiO<sub>2</sub>) nanoparticles), indicating inherent disparities in surface reactivity between these two material categories. Secondly, the increased  $H_3^+$  yield observed in faceted AuNPs, as opposed to spherical AuNPs, underscores the potential influence of surface features in enhancing surface reactivity.

### 6.4 Theoretical modeling

To gain a deeper understanding of our experimental observations, we used CTMC simulations as described in Chapter 2 in detail. The model is adapted for spherical and faceted AuNPs here. The simulations aim to elucidate the disparities observed in the momentum distributions of protons ejected from spherical and faceted AuNPs. Through this comparison, we aim to understand how the nanoparticle's geometric shape influences the characteristics of the emitted protons and the local reaction landscape resulting in the enhancement of  $H_3^+$  yields.

To simulate the near-field induced reaction yields from the surface of spherical and faceted AuNPs, the first step was to obtain the near-field distribution with the respective nanoparticles upon their interaction with laser, To do this, we used Lumerical (Ansys Lumerical 2022 R1 release, version 8.27.2898) software's finite-difference time-domain (FDTD) package. A regular mesh setting with 2 nm spacings with perfectly matched layer (PML) boundary conditions for all three dimensions is used for the simulations. We chose a dodecahedral geometry as a simplified representation of faceted AuNPs, drawing inspiration from the shapes observed in SEM images (cf. Fig. 6.1). In contrast to a regular dodecahedron, this chosen geometry features a cubic structure with edge length of 80 nm, nestled between two pyramids, with faces inclined at 60°. The selected geometry presents a favorable combination of vertices, edges, and facet features as the basis for the CTMC simulations to differentiate the individual roles of different surface elements in the observed proton momenta distribution. Here, the dodecahedron size is chosen such that the surface area is comparable to that of the 100 nm sphere.

The near-field distribution around a 100 nm gold nanosphere and the dodecahedron for two different orientations with respect to the laser polarization direction using a laser wavelength centered around 1 µm is shown in Fig. 6.4A-C. For the modeling, we used the material constants of bulk gold from Johnson and Christy [157]. Fig 6.4A shows the near-field enhancement around the 100 nm gold nanosphere, while Fig. 6.4B and C shows the near-field enhancement with the dodecahedral geometry aligned differently along the laser polarization direction. The spherical AuNP exhibited the lowest values of the nearfield enhancement factor,  $\alpha$ , while for the dodecahedron, the values of  $\alpha$  varied based on the geometric alignment along the laser polarization direction. The highest value of  $\alpha$ for the dodecahedral geometry is observed when the vertices are aligned with the laser polarization direction (Fig. 6.4B). Conversely, the near-field enhancement factor exhibited lower values when the dodecahedron is aligned in a manner where its faces align with the laser polarization direction (Fig. 6.4C). For comparison, the maximum value of  $\alpha$  obtained for the 100 nm gold nanopshere as shown in Fig. 6.4A lies around ~3.5 while for the case described in Fig. 6.4B-C, the value is ~9 and ~5, respectively.

We utilized the calculated near-field enhancement around the nanoparticle surface to induce electron ionization using Fowler-Nordheim tunneling ionization [82] for AuNPs in the present study due to their metallic nature. This is in contrast to the Ammosov-Delone-Krainov [79] ionization used for silica nanoparticles as described previously. Following the work of Murphy and Good [158] and the approximations introduced by Forbes [159] in the context of Fowler-Nordheim tunneling ionization, we employed the simple-JWKB formula to estimate the tunneling probability, expressed as:

$$D \approx \exp\left(\frac{-b_{FN}\phi^{3/2}}{E}\right),$$
 (6.1)

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where

$$b_{FN} \approx 6.83089 [\text{eV}]^{-3/2} [\text{V}] [\text{nm}]^{-1},$$
 (6.2)

and  $b_{FN}$  denotes one of the Fowler-Nordheim field emission parameters. Here,  $\phi$  represents the work function of the material, measured in eV, and E signifies the local electric field in V/nm. For our simulations, we used the work function of bulk gold ( $\phi = 5.1 \text{ eV}$ ) [157].

As electrons escape the nanoparticle, they leave behind positively charged vacancies or charges on the nanoparticle surface. The spatial distribution of these positive charges directly reflects the distribution of the laser-induced near-fields around the nanoparticle surface. To sample the location of these positive charges on the nanoparticle's surface, we employed Monte Carlo rejection sampling method. The method yields a statistical distribution of positive charges based on the calculated ionization probabilities. Not all electrons possess sufficient energy to leave the nanosystem [55]. In our model, we have not included the electron dynamics and therefore, treated the total positive charge on the surface as an effective quantity. During laser pulse interaction, molecules present on the charged nanoparticle surface undergo dissociative ionization, resulting in proton emission. The spatial distribution of proton birth positions on the nanoparticle surface is sampled using an intensity-dependent ionization rate, denoted as  $I^n$ , following the procedure implemented for silica nanoparticles previously. Here, the value of n is set to 5, aligning with experimental results due to the unavailability of the ionization potential of citrate molecules in literature. This is combined with a radial Gaussian centered around the nanoparticle's surface, characterized by a standard deviation,  $\sigma = 10 \,\mathrm{nm}$ , which accounts for the spatial arrangement of molecules surrounding the nanosurface. Despite the rapid decay of near-field amplitude with distance from the nanoparticle surface, the results remain robust against variations in the standard deviation. Protons are subsequently propagated from their respective birth locations around the nanoparticle surface using classical equations of motion, ultimately yielding the final 3D momentum spectra. In our model, we assume protons start with zero initial momentum, and their subsequent behavior is primarily influenced by electrostatic interactions with the charged nanoparticle surface. As a result, the dynamics of the emitted protons are determined by the electrostatic field generated by the positively charged surface. Additionally, we consider the Coulomb interactions between the rapidly escaping electrons and the ions ejected from the nanoparticle to have a negligible effect on the final proton momenta.

The observed differences in the near-field enhancement factor across different geometries and orientations (Fig. 6.4A-C) have profound implications for the ionization dynamics of AuNPs. Simulated proton momentum distributions corresponding to these configurations (Fig. 6.4E-F) provide crucial insights into the underlying mechanisms. The variations in proton momentum distribution (Fig. 6.4E-F), stemming from different alignments of the dodecahedral structure along the laser polarization direction, can be attributed to differences in the distribution of local surface charges. Specifically, the presence of vertices and edges induces stronger local electric fields due to their high curvature. Consequently, when the dodecahedron is aligned with its pointed vertices along the laser polarization direction, a higher local surface charge density is induced by the laser, contributing to the



Figure 6.4: (A)-(C) Simulated near-field enhancement pattern for 100 nm spherical (A) and dodecahedral AuNPs (B-C) respectively using a laser wavelength centered around 1 µm. Panel (B) and (C) illustrate two distinct orientations of the dodecahedral AuNPs relative to the laser polarization along the y-direction. In (B), the AuNP is aligned along its most pointed vertices, resulting in maximum near-field enhancement for this orientation. Conversely, in (C), the AuNP has its two opposite flat faces aligned with the laser polarization direction, leading to a lower-field enhancement. (D-E) The corresponding simulated proton momentum distribution for the geometries and orientations described in (A-C), respectively.



Figure 6.5: Simulated average distribution of proton momenta for the dodecahedral geometry of AuNP comprising of 100 different orientations relative to the laser's polarization direction.

observed higher proton momentum (Fig. 6.4E). In contrast, facets exhibit lower electric field enhancement and localization due to the absence of significant surface curvature, resulting in fewer laser-generated surface charges. Consequently, this leads to a lower local surface charge density, causing protons emitted from such locations to experience lower Coulombic repulsion from the surface, thereby yielding a lower momentum distribution (Fig. 6.4F). The model utilizes the distribution and quantity of surface charges as a key factor governing the final proton energy. While their spatial distribution closely follows the near-fields, the number of charges is introduced as a free parameter. It is determined by fitting the proton momentum distribution for the spherical AuNP case, employing a similar approach as implemented for silica nanoparticles in previous studies [63, 93].

In the simulations, we employed a constant surface charge of 800*e* for all three cases (Fig. 6.4D-F), which qualitatively was able to reproduce differences in proton momentum based on the birth positions of protons relative to local surface features. However, a more complete picture would involve considering a varied surface charge amount based on the differential values of the near-fields around the nanoparticle surface. These differences depend on factors such as the intensity of the laser experienced by the nanoparticle in the focal volume or its orientation along the laser polarization direction. The simulation results show that protons originating from a spherical geometry (Fig. 6.4D) display greater momentum values when compared to a dodecahedral geometry aligned with its square faces along the laser polarization (Fig. 6.4F). However, these values are lower when the nanoparticle is oriented along its pointed vertices (Fig. 6.4E). Fig. 6.5 shows the distribution of the simulated proton momenta averaged over 100 different orientations of the dodecahedral geometry relative to the laser's polarization direction. The spectrum doesn't reveal a double ring structure as observed in the experimental case (Fig. 6.2B), but a broad distribution of the proton momenta bounded by the two extremes as observed in Fig. 6.4E and F. Upon

comparing these observations with experimental results depicted in Fig. 6.2A-B, it is evident that the outer ring of proton momenta (Fig. 6.2B) associated with faceted AuNPs is similar to the proton momenta values observed with spherical AuNPs (Fig. 6.2A). The origin of the observed inner ring structure in the proton momentum distribution in faceted AuNPs is still unclear and necessitates further studies.

# 6.5 Ellipticity and wavelength dependence of surface yields

To investigate the influence of surface features on the formation of  $H_3^+$  ions further, we employed circularly polarized laser pulses. Previous studies via theoretical modeling have shown that when the order of nonlinearity for nanoparticle surface ionization is less than that for the dissociative ionization of surface adsorbate molecules, the angular distribution of observed protons closely mirrors the near-field angular distribution [46]. This suggests a strong correlation between near-field and ion momentum distributions for elliptically or circularly polarized laser pulses. Consistent with previous findings with spherical dielectric silica nanoparticles, the projection of the measured three-dimensional proton momentum distributions onto the polarization plane for circular polarization generated from the ionization of citrate-capped faceted AuNPs, also revealed a ring-like pattern in the distribution of high momentum protons. This pattern is depicted in Fig. 6.6A.



Figure 6.6: (A)-(B) Measured proton and  $H_3^+$  ion momentum distribution with circularly polarized laser pulses, respectively.

The low-momentum inner ring pattern with protons is also observed with circularly polarized laser pulses, similar to the linear polarization case. However, for  $H_3^+$  ions, the ion momentum distribution exhibited an angular momentum distribution that deviated from the laser's ellipticity (Fig. 6.6B) slightly. Compared to the linear polarization case (Fig. 6.3B) where the emission of the ions still follow the directionality of the laser fields, the  $H_3^+$ 



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Figure 6.7: Bar histograms comparing ion yields for selective fragments as a function of (A) laser ellipticity (linear vs. circular polarization), and (B) laser wavelength  $(1 \,\mu m \, vs. 2 \,\mu m)$ .

momentum distribution with circular polarization displayed a more isotropic distribution while also revealing a subtle dipolar signature. This observation suggests a variation in the underlying nanoparticle reaction landscape contributing to the formation of  $H_3^+$  ions. The formation of  $H_3^+$  ions appears to be significantly associated with the non-uniform charge localization around the nanoparticle surface due to the presence of distinct surface features. The presence of facets on the AuNPs leads to a varying degree of charge localization around the nanoparticle surface, particularly enhanced at vertices and edges. The localized charge interactions around such structures likely play a crucial role in promoting the formation of  $H_3^+$  ions on strong-field ionized faceted AuNPs.

Figure 6.7A presents the relative difference in the ion yields of the hydrogen ions (H<sup>+</sup>,  $H_2^+$  and  $H_3^+$ ) for faceted AuNPs with linearly and circularly polarized laser pulses. The bar graph clearly shows an increase in  $H_3^+$  yields for circular polarization compared to linear polarization. Considering that the angular distribution of  $H_3^+$  ions remains more or less consistent regardless of the laser pulse polarization, the observed increase in ion yields with circular polarization suggests that more of the surface features, particularly the edges and vertices of the nanoparticles, are influenced when circular polarization is utilized. This results in higher yields despite an overall decrease in laser intensity compared to linear polarization. This observation is consistent with the hypothesis that  $H_3^+$  formation is preferentially localized around the edges and vertices of the nanoparticles, which still experience enhanced charge interactions due to their high curvature, even with lower overall intensity.

Another interesting feature is observed when laser pulses centered around a wavelength of  $2 \,\mu\text{m}$  were utilized in the experiment. A higher yield of  $\text{H}_3^+$  ions is observed with  $1 \,\mu\text{m}$  wavelength compared to the yields recorded at  $2 \,\mu\text{m}$  despite a much higher signal observed



Figure 6.8: (A)-(B) Measured proton and  $H_3^+$  ion momentum distribution with 2 µm laser pulses, respectively.

for  $H_2^+$  ions in the latter case as shown in Fig. 6.7B. Moreover, the proton momentum distribution at 2 µm lacked a significant number of lower momentum protons, as depicted in Fig. 6.8A, contrasting with the 1  $\mu$ m scenario presented in Fig. 6.2B. The H<sub>3</sub><sup>+</sup> ions exhibited a distinct dipolar emission in the momentum distribution in the  $2\,\mu m$  case with higher ion energies. FDTD simulations for the dodecahedral geometry with a 25 fs, 2 µm laser pulses revealed a lower degree of near-field enhancement compared to the 1 µm laser wavelength as shown in Fig. 6.9. The stronger electric fields observed with the 1 µm wavelength further support the previous observation that high charge densities, resulting from these fields, favors the formation of  $H_3^+$  ions. However, the static-field model fails to capture the observed differences in the proton momentum distribution concerning the origin of the low-momentum protons or their diminished yields with 2 µm laser wavelength. This discrepancy likely arises from the model's inherent simplicity and the assumptions made regarding the ionization process. These observations highlight the limitations of staticfield models in fully describing the complex ionization dynamics of faceted nanoparticles under strong-field laser irradiation as a result of differences in their plasmonic activity with different laser wavelengths. Capturing the interplay between plasmonic interactions, nearfield enhancement, surface features, and specific ion formation mechanisms likely requires more sophisticated theoretical frameworks that go beyond the scope of this present thesis.

# 6.6 Nanoparticle size-dependent variation in surface yields

Understanding how surface features change with nanoparticle size is crucial. This knowledge gap can be bridged by studying size-dependent behavior, potentially leading to a better understanding of size-dependent catalytic activity in AuNPs [160]. Larger nanoparticles, with their well-defined facets, might offer more distinct catalytic sites compared to



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Figure 6.9: Simulated near-field distributions around a dodecahedral AuNP for laser pulses centered at (A)  $1 \mu m$ , and (B)  $2 \mu m$  wavelengths. The color scale represents the field enhancement factor.

smaller nanoparticles with a more integrated surface. This could potentially affect the reaction pathways and overall catalytic activity. While the exact mechanisms in catalysis are more complex, our findings suggest that the interplay of surface features and their spatial distribution might play a crucial role as discussed in this section.

Figures 6.10A and B depict the measured proton momentum distributions for 50 nm and 10 nm faceted AuNPs, respectively. We observe that the proton momentum distribution for 50 nm faceted AuNPs (Fig. 6.10A) closely resembles that observed for the 100 nm faceted AuNPs (Fig. 6.2B), exhibiting a high-momentum dipolar structure along with a lower momentum ring. However, upon reducing the AuNP size to 10 nm (Fig. 6.10B), the lower momentum ring appears to have vanished. This difference might be due to the varying influence of surface features based on the nanoparticle size. In larger nanoparticles, facets, edges, and vertices are typically more pronounced and spatially separated compared to smaller ones. These pronounced features in larger particles can lead to distinct electric field distributions and altered localized charge interactions, which could significantly influence ion emission dynamics. For smaller AuNPs, while surface features are still present, they are less prominent, and their influence on the electric field and localized charges might be less pronounced, potentially leading to a more uniform momentum distribution in the emitted ions. Additionally, the proton momenta are observed to decrease with a reduction in nanoparticle size, evident when comparing Fig. 6.10A with Fig. 6.10B. This decrease in proton momenta correlates directly with the diminishing Coulomb force experienced by the departing protons, attributed to a reduction in overall surface charges as the surface area decreases with the diminishing size of the nanoparticles.

Figure 6.11A presents a two-dimensional histogram of time-of-flight (TOF) versus position focusing on the hydrogen ions (H<sup>+</sup>, H<sub>2</sub><sup>+</sup> and H<sub>3</sub><sup>+</sup>) for faceted AuNPs of three different sizes: 100 nm, 50 nm, and 10 nm. The y-axis represents the position coordinate along



Figure 6.10: (A)-(B) Measured proton momentum distribution for 50 nm and 10 nm faceted AuNPs, respectively.

the laser-polarization direction. The spectrum is selectively filtered on ions emitted with high-momentum protons to highlight fragment yields from vertices and edges. Larger surface areas associated with bigger nanoparticles can lead to higher overall yields, even if the intrinsic activity per unit area is the same. This selection is aimed to isolate the true contribution of surface features (independent of size) to the observed yield. The increase in yields for  $H_2^+$  and  $H_3^+$  fragments with decreasing AuNP sizes is evident, highlighted by the pink dashed box enclosing the  $H_3^+$  ions. The quantitative analysis of this reduction in fragment yields, specifically concerning the formation of  $H_3^+$  as a function of nanoparticle size, is presented in Fig. 6.11B. Protons emerge as the most abundant fragment species for all three sizes, followed by  $H_2^+$  and then  $H_3^+$ , as evident in the figure. As the nanoparticle size diminishes, there is a noticeable increase in the yields of  $H_2^+$  and  $H_3^+$  relative to protons. A significant difference for  $H_3^+$  fragments is visible between the 100 nm and 10 nm nanoparticles. On another note, the observed asymmetry in the measured fragments, primarily visible for the proton distribution along the TOF axis, is attributed to a decrease in detector efficiency for ions arriving later within a mass peak. This reduction in efficiency occurs when ions hit the detector within the recovery time of the microchannel plate.

The observed increase in  $H_3^+$  yields with decreasing AuNP size suggests a direct correlation between nanoparticle size and reactivity. As AuNPs decrease in size, several factors contribute to this enhanced reactivity. Firstly, the higher surface-to-volume ratio in smaller nanoparticles translates to a greater number of exposed, catalytically active sites per unit volume. These sites can interact more efficiently with reactant molecules, promoting  $H_3^+$  formation. Secondly, unlike larger nanoparticles where field enhancement is localized around edges and vertices, smaller particles exhibit enhanced electric fields across a significant portion of their surface due to their high curvature. These stronger electric fields can, in turn, influence the distribution of charges on the surface, potentially leading to higher local density of surface charges and facilitating denser localized charge interactions. This combination of increased exposed catalytically active sites and enhanced charge



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Figure 6.11: (A) Measured time-of-flight (TOF) spectra of the hydrogen ions  $(H^+, H_2^+)$  and  $H_3^+$  as a function of the *y*-position of ion fragments emitted from surface molecules on differently sized nanoparticles. The ions recorded in coincidence with the low-momentum protons are filtered out in order to eliminate any surface area dependency from the analysis with variation in nanoparticle size. The dashed box in panel (A) highlights the occurrence of  $H_3^+$  and the corresponding increase in yield as the nanoparticle size decreases. (B) The hydrogen ion yields for different AuNP-sizes. The data was obtained by filtering the hits originating from the facets as shown in (A). The yield is normalized to the total number of counts of all the fragments shown for the respective nanoparticle size after filtering and shown in logarithmic scale.

interactions on smaller nanoparticles ultimately promotes surface reactions that contribute to increased  $H_3^+$  formation.

Quantitatively elucidating the processes underlying the generation of  $H_3^+$  in our study poses a challenge, as existing theoretical models are insufficient to capture the intricacies of the phenomenon. Developing a theoretical framework requires a comprehensive understanding of the dynamics associated with laser-field-induced ionization and fragmentation of citrate molecules under strong field irradiation adhered to nanoparticle surfaces. In the absence of robust theoretical approaches, we rely on a qualitative interpretation of our experimental observations. Here, we propose a mechanism focusing on the interplay between localized charge and surface features, potentially explaining the observed increase in  $H_3^+$  yield with faceted AuNPs. The differences likely arises from the distinct surface interactions involved. Drawing parallels with observations in gas-phase organic molecules under intense irradiance and bimolecular reactions on silica nanoparticle surfaces with water molecules [53], we can delineate the underlying mechanism. In gas-phase experiments, organic molecules exhibit a two-step mechanism whereby H-atom migration leads to the formation of neutral  $H_2^+$ , which subsequently captures a proton through a roaming mechanism, resulting in the generation of the trihydrogen cation. Conversely, on silica surfaces, H-atom migration within water molecules facilitates proton extraction from adjacent water molecules, facilitated by the charged silica interface. In contrast, the arrangement of citrate molecules on AuNPs differs, forms a monolayer distinct from the aggregation of water molecules on silica surfaces. The mechanism driving the formation of  $H_3^+$  ions on citrate-capped AuNPs under strong-field ionization involves a combination of factors, with charge localization emerging as the primary influence, augmented by the arrangement of citrate molecules on the nanoparticle surface.

Upon exposure to strong-field irradiation, electrons are ejected from the AuNP surface, inducing localized surface charges and simultaneously ionizing the adsorbed citrate molecules. This interaction leads to strong electrostatic interactions among the citrate molecules and the charged nanoparticle surface. The proximity and orientation of these molecules, influenced by steric effects, further enhance their interaction potential. These enhanced interactions promote inter- and intra-molecular hydrogen migration, facilitating the formation of  $H_2$  molecules. Subsequently, these  $H_2$  molecules roam across the nanoparticle surface, extracting protons from either the parent ion or other nearby ions. The charged surface of the nanoparticle creates a conducive environment for such reactions, providing a proton-rich surrounding that amplifies reactivity. These observations align with recent findings in sub-wavelength propanediol droplets [64] emphasizing the important role of the charged droplet surface in augmenting reactions through a similar proton-rich environment. Faceted AuNPs, characterized by increased surface features and thus enhanced charge localization, exhibit higher yields of  $H_3^+$  formation compared to their spherical counterparts. Likewise, the increased yield of  $H_3^+$  with smaller nanoparticles stems from stronger interactions between citrate molecules and the more confined charge localization on these smaller particles, optimizing  $H_3^+$  formation.

### 6.7 Conclusion

Overall, our study underscores the distinctive surface characteristics of faceted AuNPs compared to their spherical counterparts. We emphasize the significant role played by surface features in faceted AuNPs in enhancing surface reactivity, particularly evident in the formation of  $H_3^+$  and subsequent ion emission dynamics, with a particular focus on protons. Utilizing semi-classical simulations, we examined how the behavior of emitted fragments varies depending on their originating locations on the nanoparticle surface—vertices, edges, and faces—providing insights into the local environment and exploring the catalytic properties of different surface regions. The demonstrated capability of reaction nanoscopy has enabled the mapping of spatial variations in surface reaction yields based on the geometry of the nanoparticle surface. This advancement is achieved by leveraging the sensitivity of nonlinear ionization processes to surface features of metallic AuNPs under strong-field irradiation. Transitioning to single-shot imaging from the current approach of integrating observed ion momentum across various orientations of faceted nanoparticles could offer significant improvements with similar studies in future. Such an approach, along with time-resolved measurements would allow one to identify catalytic sites on a shot-to-shot basis in strong-field nanoparticle ionization experiments. It would also enable to directly

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correlate ion momentum with specific surface features, giving us a clearer understanding of the catalytic activity at individual sites. This could be a useful approach for gaining more detailed insights into catalytic processes.

Furthermore, our investigation into the  $H_3^+$  formation mechanism on citrate-capped AuNPs has unveiled a bimolecular reaction. This mechanism arises from the singular arrangement of citrate molecules forming a cohesive adlayer on the AuNP surface, modulated by steric effects around edges and vertices. The resulting strong charge localization upon strong-field ionization facilitates heightened interaction among adsorbed citrate molecules. Overall, the nanoscale environment fosters a proton-rich environment favoring various chemical transformations. Our results further demonstrate that smaller nanoparticles exhibit enhanced capabilities in promoting the formation of  $H_3^+$ , underscoring the size-dependent influence of AuNPs on their catalytic reactivity. Understanding the intricate details of morphology and size-dependent catalytic effects on AuNPs has implications for advancing green chemistry and sustainable manufacturing. This nuanced understanding of non-uniform surface characteristics and charge localization in faceted AuNPs provides valuable insights for tailoring reactivity in applications such as catalysis and sensing. It opens new avenues for manipulating catalytic processes at the nanoscale, allowing for more efficient use of resources, reduced waste, and improved energy efficiency in chemical processes.

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