‘Attoclock’ experiments on atomic and molecular hydrogen

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Abstract

The current thesis aims at benchmarking strong-field physics with the help of precision measurements performed on the simplest atomic (H) and molecular (H₂) systems.

The importance of H in validating strong-field models is demonstrated through the first set of experimental data. It aims at calibrating the absolute Carrier-envelope phase (CEP) of few-cycle laser pulses using H against complete \textit{ab initio} solution of the three dimensional time-dependent Schrödinger equation (3D-TDSE). Subsequent set of measurements with noble gases against widely used strong-field models based on single-active electron (SAE) approximation, is shown to reveal a systematic offset of $\sim 0.25\pi$ radians in tagging CEP, questioning the validity of such models.

The second experimental study forms the main result of this thesis, that attempts to resolve the ongoing debate on tunnelling times (tunnelling delays in the context of strong-field physics). We address this by employing the ‘attoclock’ technique with 6 fs pulses on H and validating the results against full numerical solutions of \textit{ab initio} 3D-TDSE. The validated numerical codes are then used to artificially screen the parent ion-electron interaction, concluding that the tunnelling time $\leq 1.8$ as.

The final experimental results presented in this dissertation are the alignment-dependent attoclock measurements using both few-cycle (7 fs) and multi-cycle (28 fs) pulses on H₂. The measured attoclock observable for various molecular orientations (in laser polarisation frame) shows a strong modulation with a periodicity of $\pi$. Initial \textit{ab initio} simulations for few-cycle pulses under the frozen-nuclei and SAE approximations, fail to explain these observations. Further experimental studies with H₂/D₂ (50:50 mixed gases) show no significant relative differences among the attoclock observables, suggesting a prominent role of the electron-electron correlations at play. The ongoing study is believed to have far reaching implications in applications such as studying molecular dissociation processes and tomography.
Declaration of Authorship

I, Satya Sainadh Undurti, declare that this thesis titled, “Attoclock’ experiments on atomic and molecular hydrogen ’ has not previously been submitted for a degree or diploma in any university. To the best of my knowledge and belief, the dissertation contains no material previously published or written by another person except where due reference is made in the dissertation itself.

Signed: 

__________________________________________

Date: 24 August 2018
“There are two possible outcomes: if the result confirms the hypothesis, then you’ve made a measurement. If the result is contrary to the hypothesis, then you’ve made a discovery.

—Enrico Fermi

“The working theoretical physicist is not to be envied, because Mother Nature, or more precisely an experiment, is a resolute and seldom friendly referee of his work. She never says ‘yes’ to a theory, but only ‘maybe’ under the best of circumstances, and in most cases simply ‘no.’ If an experiment verifies a theory, it is still a ‘maybe’; if it doesn’t, it is a ‘no.’ ”

—Albert Einstein
None can succeed alone! Whatever little success I may have tasted in my life, is a result of the help and support I received from many. At this juncture, I would like to thank them before I wait to segue into the next phase of my career.

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Abstract ii

Declaration of Authorship iii

Acknowledgements vi

1 Strong-field physics and importance of H 1
   1.1 Intense lasers ............................................. 1
      1.1.1 Generation of ultra-short pulses ..................... 1
      1.1.2 Chirped-pulse amplification ........................ 3
   1.2 Intense light-matter interaction–Strong field physics .... 4
      1.2.1 Multi-photon ionisation ............................ 5
      1.2.2 Tunnel ionisation .................................... 6
   1.3 CEP and its role in strong-field physics ................... 8
   1.4 Motivation: Importance of H ............................. 9
   1.5 Absolute CEP measurements with H ....................... 10
      1.5.1 Experimental set-up .................................. 12
      1.5.2 Results ............................................. 13
      1.5.3 Conclusion ........................................... 19
   1.6 Thesis outline ........................................... 20

2 A brief history of tunnelling times 22
   2.1 Introduction ............................................... 22
   2.2 Quantum tunnelling ........................................ 23
   2.3 Tunnelling times .......................................... 24
      2.3.1 Phase times and time delays ......................... 24
      2.3.2 Tunnelling times using clocks ....................... 25
      2.3.3 Complex times ....................................... 32
      2.3.4 Feynman path-integral technique and tunnelling times . 32
3 ‘Attoclock’ and tunnelling delays 36
  3.1 Simpleman’s model and tunnelling times 37
  3.2 Attosecond angular streaking 40
    3.2.1 A review of AAS experiments 42
  3.3 Motivation for attoclock with H 47
  3.4 Summary 48

4 Experimental apparatus 49
  4.1 Introduction 49
  4.2 Ti:sapphire laser system 49
    4.2.1 Mode-locked oscillator and stretcher 51
    4.2.2 Multi-pass amplifier 54
    4.2.3 Prism compressor 55
    4.2.4 Hollow-core fiber with DCM’s set 55
  4.3 CEP stabilization 57
    4.3.1 f-2f interferometer for CEP locking 58
    4.3.2 Stabilization of CEP 59
  4.4 Pulse characterization 61
  4.5 Atomic hydrogen source 62
    4.5.1 Construction of H source 62
    4.5.2 Dissociation fraction 65
  4.6 Reaction microscope 66
    4.6.1 REMI setup 67
    4.6.2 Data processing 71
  4.7 Estimated peak intensity 72

5 Tunnelling delays in atomic hydrogen 73
  5.1 Introduction 74
  5.2 Experimental set-up 76
    5.2.1 Delivering H into REMI 77
    5.2.2 Elliptically polarised light for ‘Attoclock’ 82
  5.3 Data acquisition and analysis 83
CONTENTS

5.4 Results and discussion .............................................. 94
  5.4.1 Central idea in determining tunnelling times .............. 94
  5.4.2 Numerical simulations ......................................... 95
  5.4.3 Results ......................................................... 96
5.5 Summary .......................................................... 98

6 Attoclock studies on dissociative dynamics of H₂ .................. 99
  6.1 Introduction ..................................................... 99
  6.2 H₂ in strong fields .............................................. 100
    6.2.1 Laser induced alignment/orientation of the molecules 102
  6.3 Motivation for attoclock on H₂ ................................ 103
    6.3.1 Why alignment dependent studies using H₂? .......... 103
    6.3.2 Why attoclock? ............................................ 104
  6.4 Experimental Data .............................................. 105
    6.4.1 Multi-cycle pulses .......................................... 105
    6.4.2 Few-cycle pulses ........................................... 111
    6.4.3 Numerical simulations ..................................... 112
    6.4.4 H₂/D₂ ....................................................... 114
  6.5 Summary ........................................................ 116

7 Conclusion .................................................................... 118
  7.1 Summary of the research ......................................... 118
  7.2 Future directions .................................................. 120

A List of publications and personal contributions .................. 143

B Published articles ..................................................... 145
# List of Figures

1.1 Different channels of ionisation under intense light-matter interaction 6
1.2 CEP offset of a few-cycle laser pulse 8
1.3 Set-up for absolute calibration of CEP 11
1.4 CEP averaged energy spectra 14
1.5 Accurate CEP maps of noble gases with H calibration 16
1.6 Qualitative offset phase comparison 18
1.7 Offsets phase in CEP maps 19

2.1 Illustration of Quantum tunnelling 23
2.2 A schematic representation of the Büttiker-Landauer time model 27
2.3 An illustration of Larmor time 29
2.4 Experimental set-up for the optical Larmor clock 31
2.5 Classification of tunnelling times at a level of single Feynman path 34

3.1 Potential curves of an atom in presence of an external field 38
3.2 Idea behind attoclock using circular polarised pulses 41
3.3 Experimental data in comparison with the theoretical predictions for tunnelling times in He under strong field ionisation 44

4.1 Optical layout of FemtoPower Compact Pro 50
4.2 Schematic diagram of Oscillator 52
4.3 Pulse stretcher 53
4.4 Schematic optical layout of amplifier 54
4.5 Schematic diagram of prism compressor 55
4.6 Schematic diagram of fiber with DCM 56
4.7 CEP offsets 57
4.8 Frequency combs in $f−2f$ interferometer 58
4.9 Schematic layout of $f−2f$ interferometer 59
4.10 Schematic of an interferometric autocorrelator .......................... 60
4.11 A measurement of autocorrelator trace and spectrum of laser pulse of 
duration is 6 fs centered around 754 nm and spectral bandwidth is 
273 nm before. The Y-axis of spectrum is expressed in the natural 
logarithm (log_e) of measured power in arbitrary units. ..................... 61
4.12 Schematic of RF-discharge atomic H-source ............................... 63
4.13 Quarter-wave helical resonator ............................................. 64
4.14 Schematic of emission spectroscopy set-up for determining \mu ........... 65
4.15 Schematic layout of Reaction microscope ................................. 68
4.16 Schematic of the REMI spectrometer ..................................... 69
4.17 A schematic of two axis delay line detector ............................... 71
5.1 Schematic of attoclock ..................................................... 75
5.2 Experimental set-up for H attoclock ...................................... 78
5.3 Alignment of discharge tube through the two apertures in the H beam 
line .................................................................................... 79
5.4 H-signal in REMI ............................................................... 80
5.5 CEP effects on the direction of \E_{peak} for a circular polarised pulse .. 82
5.6 Direction of \E_{peak} for a 0.84 elliptic polarised light ..................... 84
5.7 Schematic of polarimetry ..................................................... 85
5.8 Optical polarimetry ............................................................. 86
5.9 Calibrating the polarisation ellipse in REMI’s frame of reference ... 88
5.10 Ionisation events per laser shot .............................................. 90
5.11 Coincidence filters on PMD .................................................. 91
5.12 Correcting the systematic offsets in PMD ................................. 92
5.13 Extracting angular offsets from PMD ..................................... 93
5.14 Yukawa potential .............................................................. 95
5.15 Results for tunnelling delays ................................................. 97
6.1 Different pathways of H_2 interaction in strong-fields ................. 101
6.2 Illustration of molecular alignment ........................................ 102
6.3 Momentum distribution of hydrogen ions due to different pathways . 106
6.4 Determining peak field using double ionised H^+ ....................... 107
6.5 Momentum distribution of dissociated ions and corresponding electrons 108
6.6 PMD for different orientations .......................... 108
6.7 Alignment dependent offset for \( \text{H}_2^+ \) with 28 fs pulse .......................... 110
6.8 Ion-electron momentum distributions and polarimetry with few-cycle pulses ........................................ 111
6.9 Alignment dependent offsets with few-cycle pulses .......... 112
6.10 Numerical simulations for \( \text{H}_2 \) results ...................... 113
6.11 Momentum distribution of \( \text{D}^+ \) and \( \text{H}_2^+ \) .................. 115
6.12 Alignment dependent (average) relative angular offsets between \( \text{H}_2/\text{D}_2 \) 115
List of Tables

6.1  Angular offsets from numerical simulations  . . . . . . . . . . . . . . 114
Acronyms

3D  three dimensional. 24

3D-TDSE  three dimensional time-dependent Schrödinger equation. 7, 9, 10, 15, 16, 18, 19, 21, 43, 46–48, 76, 92, 94, 95, 97, 118, 119

AAS  attosecond angular streaking. 36, 40–42, 44, 48, 49, 73, 104

AASF  Australian Attosecond Science Facility. 120

AOM  acousto-optic modulator. 52, 53, 59

APD  avalanche photodetector. 53, 59

ATI  above-threshold ionisation. 5, 9, 17, 103

CEP  Carrier-envelope phase. 1, 8–17, 19, 20, 47, 52–54, 57, 58, 60, 77, 82, 83, 92, 96, 111, 113, 114, 118

COLTRIMS  Cold target recoil ion momentum spectrometer. 43, 67, 78

CPA  Chirped-pulse amplification. 1, 3, 4, 53–55

DCM  dispersion compensating mirror. 51, 55–57

DFG  difference frequency generation. 59

FRAC  fringe-resolved autocorrelation. 61

FTIR  frustrated total internal reflected. 30, 34

FWHM  Full-width at half-maximum. 2, 8, 12, 17, 44, 62, 82, 83, 96, 111, 113

GDD  group delay dispersion. 51, 55, 57, 61

HHG  high-harmonic generation. 1, 9, 103
Acronyms

**HWP**  half-wave plate. 85, 86

**KLM**  Kerr lens mode-locking. 1–4

**MCP**  microchannel plate. 11, 70

**MD**  momentum distribution. 36, 48, 78, 89, 91, 101, 106–108, 111, 115, 119

**NSDI**  non-sequential double ionisation. 103

**PBS**  polarizing beam splitter. 54

**PMD**  photoelectron momentum distribution. 75, 83, 88, 89, 91–94, 107–116

**PPLN**  periodically poled magnesium oxide doped Lithium Niobate. 52, 53, 59

**QWP**  quarter-wave plate. 85, 86

**REMI**  reaction microscope. 21, 49, 66–69, 72, 76–81, 83–85, 87–90, 101, 105, 106, 109, 111, 115, 119, 144

**RF**  radio frequency. 12, 49, 59, 62–65, 77

**SAE**  Single-active electron. 11, 16–20, 46, 114, 116, 118–120

**SF-MFPMD**  strong-field molecular frame photoelectron momentum distribution. 20, 21, 100, 105, 119, 120

**SFA**  strong-field approximation. 7, 9, 10, 37, 42, 43, 103, 104

**SHG**  second-harmonic generation. 60, 61

**SNR**  signal-to-noise ratio. 18, 107

**SPM**  self-phase modulation. 2, 55, 57, 59

**STM**  scanning tunnelling microscope. 28

**TDSE**  time-dependent Schrödinger equation. 7, 37, 43, 95, 103, 104, 113

**TEUR**  time-energy uncertainty relation. 39, 45
**Acronyms**

**TIPIS** tunnel ionization in parabolic coordinates with induced dipole and Stark shift. 44–46

**TOD** third-order dispersion. 53, 55

**TOF** time-of-flight. 12, 66, 70, 71, 78, 80, 81, 90, 92, 105, 115

**TPSD** time and position sensitive detectors. 70

**VCO** voltage-controlled oscillator. 64, 65

**VMI** velocity-map imaging. 45

**WKB** WentzelKramersBrillouin. 26, 27
Chapter 1

Strong-field physics and importance of H

The laser was invented in 1954 and from then on, dramatic progress has been made to shorten the pulse lengths. The generation of ultra-short pulses using self-modelocked techniques like Kerr lens mode-locking (KLM) and Chirped-pulse amplification (CPA) accelerated the growth of this technology and increased the peak intensity of lasers by leaps and bounds thereafter. Today, the state of the art laser pulses with durations between four to ten femtoseconds (\(1 \text{ fs} = 10^{-15}\text{s}\)) easily reach peak electric field strengths comparable to those that bind electrons in an atom. This “strong field regime” led to phenomena such as high-harmonic generation (HHG), that led to the generation of attosecond (\(1 \text{ as} = 10^{-18}\text{s}\)) pulses.

The current chapter provides a brief introduction of how such short pulses are generated, followed by an introduction to the strong-field physics with an emphasis on the modes of ionisation, specifically tunnel ionisation. The later part of the chapter discusses how the experimental data with atomic hydrogen can be used in benchmarking strong-field physics. This is illustrated by the first experiment carried out by the author wherein the absolute Carrier-envelope phase (CEP) offsets were measured and calibrated using few-cycle laser pulses. This shall set the ball rolling for the thesis’ motivation.

1.1 Intense lasers

1.1.1 Generation of ultra-short pulses

Generation of short-pulses is possible due to the interference of wavelengths spanning a broad spectra. In order to accommodate a large number of wavelengths with a little loss, we use an optical resonator. A simple optical resonator of length \(L\) is a cavity formed by two end plane mirrors, such that a stationary field is formed due to
CHAPTER 1. STRONG-FIELD PHYSICS AND IMPORTANCE OF H

the boundary condition imposed on the electromagnetic waves. The wavelengths or the cavity modes formed shall satisfy the condition:

\[ \omega = \frac{c \pi q}{L} \]  \hspace{1cm} (1.1)

where \( c \) is the speed of light and \( q \) is any natural number that completely characterise the mode. The free spectral range of the cavity i.e. the frequency difference between two consecutive frequency is given by

\[ \frac{\delta \omega}{2\pi} = \frac{c}{2L}. \]  \hspace{1cm} (1.2)

When these different modes are in phase, they interfere constructively generating a pulse train with strong electric field oscillating around a central frequency \( \omega_0 \) that can be described as

\[ E(t) = F(t) \sin(\omega_0 t). \]  \hspace{1cm} (1.3)

here \( F(t) \) is the carrier-envelope. The repetition rate for such a pulse train would be inverse of the round trip time \( T_{\text{round}} = 2L/c \) and the separation between two pulses is \( T = 2\pi/\delta \omega \). By phase locking, modes corresponding to a large bandwidth would result in a shorter pulse and so is the peak intensity higher in such cases. This is then called as a modelocked laser. Typically gain medium like Ti:sapphire support a large gain bandwidth that can generate pulses as short as \( \sim 4 \) fs measured as Full-width at half-maximum (FWHM) in intensity centered around 800 nm. Since the pulse FWHM is comparable to that of the optical cycle, we call these as few-cycle pulses.

The outstanding discovery of a passive modelocking technique, namely, KLM [1] and its further refinements [2–5] have led to the generation of ultrashort pulses that are sub-10 fs. In this technique, a \( \chi^{(3)} \) optically non-linear medium is used which in addition causing self-phase modulation (SPM), it also has an additional non-linear refractive index depending on the intensity of the light irradiated on it,

\[ n = n_0 + n_2 I. \]  \hspace{1cm} (1.4)

\( n_2 \) is the second order refractive index that is characteristic of the medium. For sapphire the typical value is \( 3.45 \times 10^{-16} \) cm\(^2\)/W. As can be seen from the value,
lower intensities go unaffected whereas the higher intensities get influenced strongly due to the $n_2$ value, called as \textit{optical Kerr effect}. For a typical Gaussian profile intensity beam incident on such a medium, the refractive index experienced about its spatial profile would differ accordingly leading to self focussing towards the resonator axis, known as \textit{Kerr lensing}. In practice, an aperture is not required and resonator geometry is chosen so that the transverse gain profile of the laser cavity can be altered to favour self-focusing. This technique relies on refraction rather than any real saturable absorber, possessing an advantage of having very quick response. Also, self focussing can lead to smaller spot sizes leading to higher intensity and better overlap of the laser and pump beam.

1.1.2 Chirped-pulse amplification

The possibility of intense light-matter interaction was primarily due to the development of CPA technique. Although short pulses were produced, the intensity was limited to few GW/cm$^2$. This is due to the damage and distortion that can cause to the medium and the beam respectively while amplifying and extracting high intensities from the amplifier. This was no longer a problem once the CPA was demonstrated [6, 7]. In order to generate higher intensities and at the same time not to induce unnecessary non-linear effects that can damage the amplification medium, it was necessary to decouple pulse fluence (energy/area) and the intensity (power/area). High fluence is necessary to extract maximum energy but high intensity is not desirable as non-linear effects are induced by the high intensities. This was achieved by choosing the right stretcher-compressor combination. The ultrashort laser pulse is stretched temporally by $10^3 - 10^5$ times so that the intensity drops proportionally. It is then amplified and later compressed back to retrieve an amplified ultrashort pulse. Ti:sapphire crystal has a gain bandwidth that can theoretically support the amplification of pulses of less than 7 fs in duration, and therefore is suited for CPA. It also has an additional advantage of excellent thermal and optical properties and moderate saturation fluence. Due to these properties, it is possible to amplify ultrashort pulses at a few KHz repetition rates, bringing the average power to few watts [8–10]. The current thesis employs a laser that uses KLM and CPA using Ti:sapphire crystal. The amplified femtosecond pulses are further compressed
which is discussed in depth in Chapter 4.

1.2 Intense light-matter interaction—Strong field physics

KLM in conjunction with CPA can produce intense laser fields when confined in both space (focussing the beam) and time (ultrashort pulses). An intense laser field is defined through its highly non-linear nature of interaction with matter. Typical electric fields between the bound electron-nucleus is in the order of $\sim 10^{10} \text{ V/m}$, whose associated electric field is strong enough to perturb the nucleus-electron interaction. At these high intensities new types of experiments become possible. Rather than averaging the effect of the interaction over many optical periods as in the case of continuous wave lasers, the electric field now can ionise the bound electron and can directly control the ionised electron’s motion.

As mentioned above, one of the major consequences of intense laser-matter interaction is ionization. Ionisation is a widely studied phenomenon, especially in the context of a single photon or few photon absorption. The photo-electric effect explains that when an atom absorbs a photon with total energy greater than its ionization potential, the excess energy after ionisation is carried away by the free electron. However, experiments in the early 1960’s [11,12] with a strong Ruby laser with photon energy of 1.7 eV demonstrated breakdown of argon and helium gases whose ionisation potential is an order of magnitude higher than the single photon energy. The main observation of these studies were that the ionisation yield was highly non-linear with respect to the intensity of the laser, following a linear curve on a semi-log plot. The major breakthrough in understanding the intense- light matter interaction came from the seminal work of Leonid Keldysh [13]. He theorised that the ionisation processes in a strong external field could occur in two different ways: multi-photon ionisation and tunnel ionisation which are illustrated in the Fig.1.1. These ionisation processes can be parametrized through the Keldysh parameter,

$$\gamma = \sqrt{\frac{I_p}{2U_p}}, \quad (1.5)$$
where \( I_p \) is the ionization potential and \( U_p \) is the ponderomotive energy i.e. the cycle averaged kinetic energy of an electron gained in the laser field. The ponderomotive energy is given by,

\[
U_p = \frac{I}{2c\varepsilon_0\omega_0^2} = \frac{E^2}{4\omega_0^2}.
\]

(1.6)

Here \( I \) is the intensity of light field given in terms of the field \( E \) as \( I = \frac{1}{2c\varepsilon_0E^2} \), \( \omega_0 \) is the angular frequency of the laser radiation and \( \varepsilon_0 \) is the vacuum permittivity and \( c \) is the speed of light.

### 1.2.1 Multi-photon ionisation

Atoms can be ionized by radiation which has energy lesser than the ionisation potential. This is possible when an atom absorbs multiple photons simultaneously to acquire enough energy to be ionised (see Fig.1.1). The released electron has a minimum energy equal to \( E = n\hbar\omega - I_p \), with \( n \) being the minimum number of photons required to overcome the binding energy of the atom. This was first experimentally observed in the ionisation of Xenon atoms [14]. In addition to the multi-photon ionisation, they have also observed a heavily structured photoelectron spectrum that can be explained by following the relation,

\[
E = (n + s)\hbar\omega - I_p.
\]

(1.7)

The excess \( s \) photons absorbed lead to the so called ‘above-threshold ionisation (ATI)’, where the atoms absorb more photons than required for the ionization and the excess energy is carried away the electron.

When the influence of the external field is small compared to the field-free Hamiltonian, the interaction with the external field can be accounted by adding correction terms to the solutions of the field-free Hamiltonian. This is called the perturbation theory and is helpful in calculating the ionisation rates for multiphoton processes. The ionization rate is greatly enhanced if energy of the absorbed photons is equal to the ionization potential. In this approach, an \( N \)-photon ionization process can be treated by using the lowest non-vanishing order term in the perturbation
Figure 1.1: A schematic of different channels of strong-field ionisation shown (in 1D case for simplicity) with the increasing order of the field strength. The blue curve represents the (perturbed) Coulomb field in which the electron is bound and the orange line represents the external static field. (a) Multiphoton ionisation occurring by absorbing multiple photons (red arrows) such they overcome the ionisation potential. This is in the perturbative regime $\gamma \gg 1$. (b) As the external field grows in strength, the Coulomb field gets suppressed allowing the electron to tunnel through the barrier. This leads to tunnel ionisation. (c) Intensities greater than $\sim 10^{15}$ W/cm$^2$ can suppress the barrier further down than the bound state energy, leading to an over the barrier ionisation.

series [15] where, the N-photon ionization rate ($\Gamma^{(N)}$) for example is calculated as,

$$\Gamma^{(N)} = \left( \frac{I}{\hbar \omega} \right)^N \sigma^N(\omega),$$

where the first term represents the photon flux and the second term corresponds to the cross-section related to the $N^{th}$ order matrix element between initial and final states in the perturbation series. A detail analysis and explanation can be found in [15]. This approximation holds in the regime $\gamma \gg 1$ and thus defines the multiphoton ionisation regime. As the intensity is increased, higher order terms start to contribute and the perturbation expansion may not converge.

### 1.2.2 Tunnel ionisation

The $\gamma \ll 1$ corresponds to the strong field regime where the frequency of light is small compared to $I_p$, but the strength of the field is large enough to suppress the Coulomb potential. The drop in the effective Coulomb potential can result in two potential channels for ionization. The two channels for ionization are over the barrier ionization and tunnel ionization. The tunnelling regime occurs at laser frequencies low enough that the electron has time to tunnel through the barrier during one laser cycle. In this case the field suppressing the coulomb potential can be considered
static. Over-the-barrier ionization (OBI) process occurs at higher intensities than tunnelling as shown in Fig. 1.1.

The \( \gamma \ll 1 \) regime is in the non-perturbative regime \( i.e. \), the external field is strong and cannot be treated by adding a few correction terms to the field-free solutions. In this case, the time-dependent Schrödinger equation (TDSE) needs to be completely solved after the inclusion of all the required interaction terms into the Hamiltonian. A special case in the non-perturbative regime is the low frequency limit. Here, it can be assumed that the ionizing system adjusts adiabatically to the external field and the ionization yield \( Y \) can be computed using the quasi static formula that in turn uses static field ionization rates integrated over the pulse duration:

\[
Y = 1 - \exp\left(-\int_{-\infty}^{\infty} dt' \Gamma_{stat}(E(t'))\right),
\]

where \( \Gamma_{stat}(E) \) is the static ionization rate for a field strength, \( E \). In this regime the problem reduces to the time-independent problem.

Tunnel ionisation rates for the hydrogen atom were first derived in 1965 by Landau and Lifshitz [16]. This formula was generalized for complex atoms, in the single electron approximation (SEA) by Ammosov, Delone and Krainov in 1986 [17], which is commonly known as the ADK formula. According to this formula the static field ionization rate for an atom at a field strength \( E \) is given as,

\[
\Gamma_{ADK}(E) = \frac{C_l^2}{2^{2|m|}|m|!} \frac{(2l + 1)(l + |m|)!}{2(l - |m|)!} \frac{1}{\kappa^{2Z_c/\kappa - |m| - 1}} \left(\frac{2\kappa^3}{E}\right)^{2Z_c/\kappa - |m| - 1} e^{-2\kappa^3/3E}. \quad (1.10)
\]

Here \( l \) and \( m \) are the orbital and spin angular momentum quantum numbers of the outermost electron of the atom, respectively and \( \kappa = \sqrt{2I_p} \) with \( I_p \) and \( Z_c \) being the ionization potential and the effective nuclear charge respectively. \( C_l \) is the amplitude of the electron wavefunction in the tunnelling region given by,

\[
C_l^2 = \frac{\kappa}{2\pi Z_c} \left(\frac{4e}{Z_c^2/\kappa^2 - l^2}\right)^{Z_c/\kappa} \left(\frac{Z_c/\kappa + l}{Z_c/\kappa - l}\right)^{l+1/2}. \quad (1.11)
\]

Apart from the ADK model, there were several theoretical models like the empirically corrected ADK model [18], strong-field approximation (SFA) [19] wherein the interaction between the ionised electron and the parent-ion is neglected, three
CHAPTER 1. STRONG-FIELD PHYSICS AND IMPORTANCE OF H

Figure 1.2: An illustration of a CEP offset of 0 (red colour) and $\pi/2$ (blue colour) for a few-cycle laser pulse of FWHM 6fs, shown in its (a) field and (b) intensity.

dimensional time-dependent Schrödinger equation (3D-TDSE) using an effective potential in order to account for the electron-electron correlations with a dipole approximation that could be derived using various methods [20], etc. There are also other methods like the R-Matrix method [21–23] and very recently a hybrid coupled channel approach [24] was developed for finding the ionization rates for atoms and simple molecules interacting with strong fields.

1.3 CEP and its role in strong-field physics

The electric field of a few-cycle laser pulse is mathematically described as:

$$\vec{E}(t) = E(t)\cos(\omega_0 t + \phi_{CEP}),$$

where $E(t)$ is the pulse envelope and $\phi_{CEP}$ is the CEP offset between the carrier and envelope as shown in Fig.1.2. It defines the offset between the peak of the pulse envelope and the maximum of the electric field. For a phase difference of 0 and $\pi/2$ as shown with red and blue colour in Fig.1.2, a considerable difference can be observed in the field and thereby the intensity profile of the carrier field. Normally, the CEP of the laser pulse in an oscillator can drift and change from pulse to pulse. However, with the development of frequency combs, it is possible to stabilise the CEP on pulse-to-pulse basis [25] and is described in detail in Chapter 4.

Carrier-envelope phase offsets have a considerable effects on the optical processes
that directly depend on the instantaneous field of the laser pulse. By tuning the CEP one can steer the electron wavepacket and achieve desired atomic or molecular processes. Having an accurate knowledge of it can be useful in the scientific applications like HHG [26, 27], ATI [28], generation of attosecond pulses [29, 30], coherent control of molecular dynamics [31–34] etc. It was experimentally demonstrated that CEP could be tagged using Xenon atoms as target species by Paulus et al. [35]. The direction of the emitted photoelectrons was controlled by changing CEP and in turn used as a tool to determine the CEP using classical simulations [36]. These results were reported to be in good agreement with the quantum mechanical calculations using an improved SFA model [37]. However modelling atomic Coulomb potential in multi-electron systems and predicting its effects on the electron wave-packet is a major challenge even for the advanced theoretical models. Usually the CEP is extracted by the interaction of few-cycle laser pulses with atoms. The CEP obtained in this way depends strongly on the reliability of the theoretical models. Therefore, the questions remain about any possible systematic offsets that could have gone unaccounted in such measurements. We later show how an experiment with H and a comparison with the complete solution of 3D-TDSE can resolve this and can provide an accurate and extremely reliable measurements of absolute CEP.

1.4 Motivation: Importance of H

With various strong-field phenomena observed experimentally today in the labs, it is equally important to model these using appropriate physical theories. With the current models, it is difficult to understand the strong-field ionisation dynamics completely in the regimes of $\gamma \sim 1$ where the present available Ti:sapphire laser technology operates. It is necessary that, in this regime these theoretical models shall be compared to careful experiments to a very high degree of precision and accuracy in order to validate them. This also requires one to possess a complete knowledge of the experimental parameters that are fed into the theoretical models as inputs. The theoretical predictions can digress a lot from observations due to the highly non-linear nature of interaction.
In this respect, atomic hydrogen serves as a benchmarking species due to its simplest atomic structure that does not demand any electron-electron correlations, SFA or adiabaticity. The hydrogen is a physical two-body system that can be solved with arbitrary precision using 3D-TDSE (in the non-relativistic approximation) and yields solutions in closed form. It has been long known that atomic physics experiments performed with H could be used as a point of reference for our understanding of the inherently complex dynamics of light-matter interactions. Therefore, H offers unparalleled opportunities for benchmarking such experimental and theoretical techniques in strong field physics. Careful experiments on H can yield data that quantitatively agrees with the theoretical predictions to within experimental uncertainty. Both the data and the predictions are validated by such agreement.

The relevance of atomic hydrogen in benchmarking strong-field physics was demonstrated experimentally [38] and with an excellent agreement between theory and experiment, it was possible to calibrate few-cycle laser pulse intensities within an accuracy of 1% [39]. The ionisation cross sections of noble gases measured relative to H, that was already in good agreement against 3D-TDSE, were later used to create a secondary calibration standard [40]. Details pertaining to it can be found in [41].

Subsequently, we performed measurements on H and noble gases towards determining the absolute CEP of the few-cycle laser pulses. The lead experimentalist of the project was Dr. Champak Khurmi. The current chapter would discuss the details of our project in the following section as an illustration to stress the importance and necessity for experiments with atomic hydrogen in strong-field physics. In addition, this would eventually serve as a motivation for the current thesis.

### 1.5 Absolute CEP measurements with H

The aim of our experiment was to provide accurate measurements of CEP effects on ionisation of the noble gases with few-cycle pulses. This was achieved by first calibrating CEP with H and removing any possible systematic offsets. In order to observe ionisation effects on the target species, we looked at the electron energy spectrum as a function of CEP. The experimental data of H was compared against 3D-TDSE simulations (under relativistic approximation) for calibrating the CEP,
which is then used for other noble gases. The electron energy spectra for noble gases is compared with the theoretical models based on Single-active electron (SAE) approximation. The motivation of the project was not only help calibrate absolute CEP but can also help as a point-of-reference for improving theoretical models describing the complex atoms in strong fields.

Figure 1.3: Schematic of the experimental set-up for calibrating absolute CEP with H. M1-M3 are the reflective mirrors; PNDF: pellicle neutral density filters; OAP is the off-axis parabolic mirror that focusses the light beam into the interaction region; W symbolises the pair of fused silica wedges used to change CEP; TMP: turbomolecular pump keeping the system under vacuum. (b) Represents the electron TOF system measuring counts and energy of the photoelectrons. microchannel plate (MCP)s are used to detect electrons post the ionisation events and an analog-to digital card is used to acquire this signal into a computer using a LabVIEW. The interaction frame is defined at the bottom left. Adapted from [42].
1.5.1 Experimental set-up

A schematic of the experimental set-up is shown in Fig.1.3 (a). Home-built time-of-flight (TOF) mass spectrometer was used for measuring the energy spectrum of electrons. An radio frequency (RF) discharge source was used to dissociate H\textsubscript{2} to H and was used as the target species integrated with the TOF system. The laser pulses of central wavelength 780 nm, FWHM of $\sim$ 6 fs at repetition rate of 1-kHz were generated from a commercially available few-cycle laser system, Femtopower Compact Pro CEPPhase Stabilised. An additional $f - 2f$ interferometer (Menlo Systems) was used to provide a constant feedback and locking at 1 kHz frequency near the experimental end-station. The CEP was changed in a controlled manner ranging beyond $2\pi$ using a set of matched fused silica wedges (MolTech GmbH) on a motorised translation stage such that a lateral translation of 1 mm equals 1.25 rad of phase shift. A detailed description of the femtosecond laser system, CEP locking technique and atomic H source is provided in Chapter 4. The laser gets focussed (spotsize, $w_0 \approx 45 \mu$m and Rayleigh length, $z_R \approx 10$ cm) using an off-axis parabolic mirror of focal length 75 cm in the interaction region (TOF system) and the intensity was changed using pellicle neutral density filters. The target atoms reach the TOF system through a UHV beam line placed perpendicular to the laser beam. Electrons generated from the interaction were detected using the TOF system.

Since the atomic beam is perpendicular to the laser beam line, it is possible for the atoms to see different regions around the focal spot along the beam propagation, thereby seeing a change in Gouy phase. Gouy phase at a point $z$ distance away from the focal spot is given by $\phi_{\text{Gouy}} = \tan^{-1}(z/z_R)$, with $z_R$ being the Rayleigh range. For an ideal Gaussian beam, the CEP too changes through Gouy phase as $\phi_{\text{CEP}}(z) = \phi_{\text{CEP}}(0) + \phi_{\text{Gouy}}$ [38]. Hence, depending on the spread of the interaction region around focal spot, it is necessary to average the effect of Gouy phase. We avoid this by ensuring that the atomic beam diameter is $\sim 0.5$ mm $\ll 10$ cm ($z_R$). Hence the change in the Gouy phase is only $\Delta \phi_{\text{Gouy}} \approx \pi 0.5/100$, which is 17 mrad that is an order of magnitude small compared to the CEP noise of 300 mrad.

A schematic of the TOF detection system is shown in Fig.1.3(b). The principle behind any mass spectrometer relies on the fact that charged particles of identical charge ($q$) with same initial speeds attain same kinetic energy when accelerated in a
uniform electric field, irrespective of their mass $m$. However, the time taken by each particle depends on its charge to mass ratio such that $t \propto \sqrt{m/q}$. The entire TOF system is kept under ultra-high vacuum. The system was encased in $\mu$-metal to keep it unaffected from any external stray fields. The interaction region was between two grounded electrodes placed 10 mm apart. Though the plates are grounded the energy electrons possess are enough for them to reach the detector. The two electrodes are flat plates of size $5 \times 5$ cm and the bottom one had a diagonal slit ($5 \times 1.7$ mm) that made it easier to align laser beam to the gas jet. The microchannel front plate placed below the slit at $\sim 105$ mm was kept at a positive voltage of $\sim 300$ V using an external power supply Kepco APHM500M accelerating the electrons entering through the slit. A voltage difference of 1700 V was maintained between the front and back plates of MCP that enable to create secondary electrons. The MCP (Hamamatsu F9890–31) was a dual chevron assembly with an efficiency of $1:10^6$ and has a diameter of 27 mm. These secondary electrons are then further accelerated by an anode put at 500 V higher voltage using another power supply Matsusada ES–501.2. Each bunch of electrons create a temporally resolved voltage spike by using an analog-to-digital converter (A/D) card (Agilent U1084A Acquiris) working at a 250 ps timing resolution with 8 bit resolution. The data was acquired using a LabVIEW program and stored into a PC simultaneously. A detailed description of the nuances of construction and data acquisition can be found in [41].

1.5.2 Results

We use a linear vertically polarised laser pulses to confine electrons in the plane of TOF. The laser not only ionises the target species but also background gases present in the interaction chamber. In case of atomic H beam, it consists of residual H$_2$ too. Since we are interested in electrons and the TOF mass spectrometer could not perform any coincidence measurements of ion-electrons, it was necessary to perform a background subtraction. Hence, at each intensity, three CEP resolved measurements of yield as a function of energy and CEP ($Y(E, \phi)$) were taken in case of H; (i) discharge ON (H+H$_2$+background, $Y^{ON}(E, \phi)$) (ii) discharge OFF (H$_2$+background, $Y^{OFF}(E, \phi)$) and (iii) only background ($Y^{bck}(E, \phi)$) by not letting the gas into the interaction chamber with closing a gate valve. Finally the electron energy spectrum
CHAPTER 1. STRONG-FIELD PHYSICS AND IMPORTANCE OF H

$Y(E, \phi)$ considered was

$$Y(E, \phi) = (Y^{ON}(E, \phi) - Y^{bck}(E, \phi)) - (1 - \xi) (Y^{OFF}(E, \phi) - Y^{bck}(E, \phi)),$$  

(1.13)

where $\xi$ is the dissociation fraction. Whereas for the noble gases, two measurements were taken i.e. (ii) and (iii) such that

$$Y(E, \phi) = (Y^{ON}(E, \phi) - Y^{bck}(E, \phi)).$$  

(1.14)

This was repeated at every CEP value therefore removing the systematic offsets arising from the non-target species or the background.

\[\text{Figure 1.4: CEP-averaged energy spectra for different targets as specified in the legends for (a) } 1.2 \times 10^{14} \text{ W/cm}^2 \text{ and (b) } 2.5 \times 10^{14} \text{ W/cm}^2. \text{ The yield curves as a function of energy } Y(E, \phi) \text{ are plotted in log}_{10} \text{ scale (shown in arbitrary units) and relative offsets are added to make it easy to distinguish while viewing. The figure is taken from [42].}\]

At every position of wedge i.e. CEP, the electron energy spectrum $Y(E, \phi)$ was collected for 90 seconds (for each measurement in the set to determine $Y(E, \phi)$). The photoelectron yield is highly energy dependent and a CEP averaged energy spectra for different gases look as shown in Fig.1.4. The measurements were performed at two intensities: $1.2 \times 10^{14}$ W/cm$^2$ ($U_p = 7 \text{ eV}, \gamma_H = 0.98, \gamma_{Ar} = 1.06, \gamma_{Kr} = 1, \gamma_{Xe} = 0.67$) and $2.5 \times 10^{14}$ W/cm$^2$ ($U_p = 15 \text{ eV}, \gamma_H = 0.98, \gamma_{Ar} = 0.72, \gamma_{Kr} = 0.68, \gamma_{Xe} = 0.64$). In
order to parametrise the effects of CEP, the energy spectrum used was:

\[
S(E, \phi) = \frac{Y(E, \phi) - Y(E, \bar{\phi})}{Y(E, \bar{\phi})},
\]

where \(Y(E, \bar{\phi})\) is the laser CEP-averaged energy spectrum. Therefore, \(S(E, \phi)\) measures the effect of CEP at energy \(E\) relative to the averaged CEP electron yield.

The CEP maps \(S(E, \phi)\) are shown in Fig.1.5(a) and (b) for lower and higher intensity regimes, respectively. The intensities during this experiment were estimated from first principles using laser focus spot size, average power and pulse width measured using an intensity interferometric autocorrelator. Figure.1.5(a) and (b) shows the CEP maps of the measured electron energy spectra (top panels) against the theoretical data in the bottom panels. The energy axes is labelled in units of eV (bottom) and \(U_p\) (top). The CEP was gradually changed in a span of 0 to \(2\pi\) and this data was replicated from \(2\pi\) to \(4\pi\). As shown in our previous work [40], reliable \textit{ab initio} 3D-TDSE simulations were provided by collaborators Dr. Igor Ivanov and Prof. Anatoli Kheifets in calibrating CEP with H. The experimental results for H can be considered quite reliable as it is evident from the good agreement found in the data comparing energy spectrum \(\geq 2U_p\) for H.

The electrons can be distinguished as high or low energy electrons at \(2U_p\) energy. The energy attained by electrons in these two domains are from different interactions. Low energy electrons \((< 2U_p)\) are the direct electrons ionised at a any phase of the pulse (although the probability is highest at the peak of the pulse), leading to a modulation in the energy spectrum as a function of CEP. On the other hand, the high energy electrons \((> 2U_p)\) are the rescattered electrons from the parent ion. In this domain, the energy of the electrons depend on the peak electric field of the pulse with its yield depending on the peak field strength before the largest one [43]. In addition, the laser CEP dependence on the energy is more stable than at the low energy domain and therefore used this domain to calibrate the CEP with H.

As the CEP-stabilisation system can only give us the information of relative variation in CEP and not the absolute value, we had to initially overlap the CEP map of H obtained experimentally to the theory to remove any systematic offsets. But due to the fact that the beam waist is non-zero, the intensity changes spatially around the focus and hence total ionisation yield shall be calculated over the intensity distribution.
Figure 1.5: CEP maps for noble gases Ar, Kr and Xe measured by first calibrating absolute CEP using H. (a) are measurements taken at $1.2 \times 10^{14}$ W/cm$^2$ and (b) are at $2.5 \times 10^{14}$ W/cm$^2$. The top panel in both (a) and (b) are experimental results, while the bottom panel are theoretical simulations. 3D-TDSE was used for H and models based on SAE were used to calculate CEP maps for noble gases. The photoelectron energy in the bottom axis is expressed eV and the top axis is in units of $U_p$. Figure adopted from [42].

This is important for a proper comparison between theory and experiment and called as focal volume averaging. Ionisation probabilities–$P(I_0, \phi_{CEP})$–is provided from theorists for various peak intensities and CEP values. We then integrate the
ionisation probability spatially considering various intensity contours to find focal volume averaged-ionisation probability $P_{FVA}(I_0, \phi_{CEP})$. Since $z_R \gg w_0$ we avoid averaging Guoy phase and therefore consider $\phi_{CEP}$ to be constant in the focal volume. Due to radius of atomic beam $r \gg w_0$, the focal volume is modelled as a cylindrical volume with radius $w_0$ and length $r$. The cylindrical geometry allows us to find the following relation

$$P_{FVA}(I_0, \phi_{CEP}) \propto \int_{-\infty}^{\infty} P(I_r, \phi_{CEP}) r^2 dr \quad \text{with} \quad I(r) = I_0 e^{-2r^2/w_0^2}, \quad (1.16)$$

where $I(r)$ is a Gaussian radial distribution of intensity around focus. Both the experimental and theoretical data was smoothed using a Gaussian filter with a FWHM of 1.5 eV for ease of viewing. We remove systematic offsets by comparing experiment and theory for H.

Now that CEP is calibrated and subsequently the measurements were done on noble gases, we can therefore assign absolute CEP to this data that is free of systematic errors. The \textit{ab initio} simulations for noble gases was provided by Prof. Xiao-Min Tong. The ATI spectra were calculated using generalised spectrum in the energy representation \cite{43,44} under SAE approximation using model potentials \cite{32} obtained by density functional theory with the self-interaction correction \cite{45}.

From the experimental data it is evident that there is a clear systematic offsets observed in the CEP maps of experimental data on its comparison with widely used theoretical models based on SAE. In order to quantify the systematic phase offsets, the data in Fig.1.5 was chosen above $2U_p$ that was used to calibrate CEP and projected it on the CEP axis at energy $E$, $B_E(\phi)$. One shall expect a modulation as a function of CEP $\phi$ from the theory data. We fitted this data using a simple sinusoidal function with fitting parameters $A$ and a systematic offset $\phi_0$ using an analytical fit

$$B_E(\phi) = A \sin(\phi + \phi_0). \quad (1.17)$$

The Fig.1.6 shows the offset phase $\phi_0$ as given in Eqn.(1.17) at energy $E$, for electrons with energy $\geq 2U_p$. The black line shows experimental data while the red line shows the theoretical prediction of the offset phase. Qualitatively a good agreement is found between theory and experimental data for H at higher intensities.
In Fig. 1.6(b). A clear offset phase of at least $0.25\pi$ can be observed in case of noble gas atoms between SAE theory and experimental data in Fig. 1.6(d),(f) and (h). In case of lower intensity shown in the left column, the 3D-TDSE data agrees better with the data in the region $E \geq 3U_p$. The lower energy domain below $3U_p$ suffers from a bad signal-to-noise ratio (SNR) giving rise to large modulations around the predicted offset phase. This can also be seen in the offset phase plots for noble gases in Fig. 1.6(c),(e) and (g). Hence only a qualitative observations could be made unlike in the case of higher intensity.

Better quantitative analysis was done by binning the energy into appropriate bins chosen by optimising and compromising on both SNR and the energy resolution. An optimal bin size of 5 eV was chosen and the offset phases was plotted for different targets. The plots shown in the left column are for the low intensity $1.2 \times 10^{14}$ W/cm$^2$...
Figure 1.7: Plots (a) and (b) show experimental offset phases for experimental data with 5 eV energy binning for various species as mentioned in the legends. Plots (c) and (d) show the relative offset phases between theory and experiment with 5 eV energy binning. The left column (a) and (c) are for lower intensity and the right column represent data for the higher intensity. Note that the offset phases here are in radians. Figure adopted from [42].

and the right column is for the higher intensity range $2.5 \times 10^{14}$ W/cm$^2$. We see a relative offset phases in the experimental data for different targets in Fig. 1.7(a)-(b). The below row shows a relative offset phases between experiment and theory. It is evident that a good agreement is found between 3D-TDSE and experimental data for H in both intensity regimes. For the noble gases, contrary to the SAE simulations, the observed CEP maps for energy $E \geq 2U_p$ depend on the photoelectron energy. In addition to this, considerable amount of systematic offsets are present between the measured offset phase and the SAE models predictions, showcasing the shortcomings of these models and their usage in calibrating absolute CEP.

1.5.3 Conclusion

The systematic offsets observed in CEP maps with noble gases could only be possible due to the experimental evidence from H calibration. A direct theoretical comparison between SAE for noble gases and 3D-TDSE for H could not have concluded the
same, since one cannot definitively isolate the contributions due to approximations considered in the model to that of the true systematic offsets. It is not trivial to interpret the physical phenomenon responsible for the complex CEP resolved photoelectron energy spectra measured. Any such attempts to assign a particular mechanism responsible for observed spectra would heavily depend on the key theoretical assumptions in estimating atomic Coulomb potential, electron rearrangement dynamics after light absorption, and the effect of long-range Coulomb potential on the electron wave packet before it hits the detector. We used the extremely reliable and accurate measurements of the phase offset in H-referenced noble gases that could expose the weakness of theoretical models based on SAE approximations. Our experimental results clearly demonstrate that one cannot rely completely on approximate theoretical methods such as SAE to accurately calibrate the CEP of the few-cycle laser pulses using noble gases. Conversely, it is also true that given we have the laser parameters as inputs, such models cannot model the strong-field phenomena accurately.

1.6 Thesis outline

With the same motivation as shown in the above illustration of measuring absolute CEP using H, the main results of the current thesis is to examine tunnelling dynamics using H. We specifically study the problem of 'tunnelling time' in the context of strong field ionisation using the precision measurement technique, 'attoclock'. We believe that our effort directed towards resolving the ongoing debate on tunnelling delay times and these results can be used to guide and validate all future multi-electron theoretical simulations to model the tunnelling dynamics better. We later apply this technique on the benchmarking molecular species H$_2$ to understand some interesting molecular dynamics, albeit analysing it using the strong-field molecular frame photoelectron momentum distribution (SF-MFPMD)s.

The outline of the thesis is as follows:

Chapter 2 introduces the tunnelling time concept. It further provides various definitions and attempts to measure tunnelling time in various physical platforms like semiconductor heterostructures, optics etc.
Chapter 3 provides a discussion on the semi-classical models associated with tunnel ionisation that eventually led to the inception of the attoclock to measure tunnelling times in strong field physics. A brief literature review of previous attoclock measurements is discussed with finally providing the reasons for performing attoclock with atomic hydrogen.

Chapter 4 discusses the necessary experimental set-up required for performing the experiment in the lab. This includes the few-cycle Ti:sapphire laser system used to generate femtosecond laser pulses and its characterization, the target—atomic hydrogen source and the diagnostics for the particle imaging system—reaction microscope (REMI).

Chapter 5 presents the first-ever attoclock measurement performed on atomic H. It begins with the integration of atomic H source with the REMI and the importance of elliptic polarisation for the measurement technique. Analysis of data in comparison with numerical simulations performed using 3D-TDSE is presented.

Chapter 6 presents the recent experimental data produced by performing the angular streaking technique on molecular hydrogen. The experimental data is analysed considering the SF-MFPMDs. The chapter discusses how such an analysis could be useful and have any possible implications in understanding molecular dynamics.

Chapter 7 provides some conclusion remarks and future directions of this work.
2.1 Introduction

The early twentieth century has seen the birth of two revolutionary theories in physics: theory of relativity and quantum mechanics. If the former dealt with the cosmic scales of length and energies, the latter dealt with the atomic and sub-atomic world. ‘Quantum mechanics’ is so rightly named that the quantum mechanical laws restrict its world to exist in discretized states of energy, momentum, spin etc. The word ‘quantum’ originates from the latin word ‘quanta’ meaning “how much”, reflecting this nature of discreteness. Although the origin of quantum mechanics dates back to the paper of Planck’s law of black body radiation and later photo-electric effect, it was eventually re-conceived by Erwin Schrödinger, Max Born, Werner Heisenberg among many other physicists which helped us in (re)shaping our understanding about the world the way we know. Their theories has led today to the mathematical formalism of using a complex wave-function for a particle to describe its dynamics and provides information about the probable physical observables that it can possess. This is famously often cited as the ‘Copenhagen interpretation of quantum mechanics’. Few important aspects of the theory include matter-wave duality, quantisation, non-locality, probabilistic nature of reality etc. These are quite paradoxical and counter-intuitive in their nature that according to one of the founding fathers of quantum theory, Neil’s Bohr,

“Anyone who is not shocked by quantum theory has not understood it”

Quantum mechanics with all its ‘weirdness’ is one of the very successful scientific theories produced by mankind. This also has led to the development of various applications that include light-emitting diodes, laser, transistor, superconductors, scanning tunnelling microscopes etc.
2.2 Quantum tunnelling

Quantum tunnelling is one of the key and distinctive phenomenon in nature that is very unique to quantum mechanics. It is central to many biological processes like photosynthesis to the scenarios involving electron transport in semiconductor diodes/transistors. Classically, a particle with total mechanical energy $E_n$ cannot overcome or cross a barrier $V$ if $V > E_n$. Nonetheless, in case of a quantum particle, there exists a finite probability for finding it on the other side of the barrier unless the barrier height is infinite i.e. $V = \infty$. Since the total mechanical energy (sum of kinetic and potential energy) of the particle is lesser than the potential barrier while travelling under it, the particle carries negative kinetic energy and an imaginary velocity under the barrier. Thus, we call this region as ‘classically forbidden’.

![Figure 2.1: A schematic of a quantum particle with total energy $E_n$, incident wave-function $\psi_{\text{incident}}$ tunnelling through a potential barrier of height $V$ and appearing on the other side with wave-function $\psi_{\text{exit}}$. Figure adapted from [46].](image)

Although quantum tunnelling is well understood and exploited for various applications, there is no consensus in the scientific community on “How long does it take for a particle to tunnel through the barrier?” and there is an ongoing debate regarding the meaning, interpretation and value of the ‘tunnelling time’. Quantum mechanics can calculate expectation values of a physical quantity modelled as an operator, which then can be measured in the lab. The difficulty in answering the above question partly lies in the fact that time is not considered as an operator in quantum theories unlike other physical observables. However, attempts have been made in answering this question right from the inception of the ‘tunnelling’ idea [47].
In fact there seems to exist some reconciliation among physicists regarding tunnelling times provided it can be understood in a broader perspective and different approaches can be formulated to investigate different aspects in the tunnelling process. This has led to different perspectives and various definitions which is presented in the following section.

2.3 Tunnelling times

This section introduces various definitions of tunnelling times with the physical models based on which they were conceived. The debate on tunnelling times is a major driving factor for the current project presented in this thesis, albeit in a strong-field scenario. But these concepts of tunnelling times would be revisited and adapted into the context of attoclock which will be presented later in Chapter 2.

2.3.1 Phase times and time delays

The initial notable works on tunnelling times were done by Eisenbud [48], Wigner [49] and Bohm [50]. These models are very close to the classical picture of waves getting scattered through a potential. A certain amount of phase shift is acquired when the incident waves get scattered through a potential. The ‘time-delays’ are defined as the energy derivative of this relative phase shifts ($\partial \theta / \partial E_n$) and therefore these are known as ‘phase times’. These included only the stationary (time-independent) wavefunctions and hence the methods were called stationary-phase methods. This was further generalized and a comprehensive overview of time-delays can be found in [51] and references therein. Later, Smith [52] introduced the collision life time that characterizes the duration of a collision process in three dimensional (3D). The collision life time is based on the idea that

“...the average time of residence in a region is the integrated density divided by the total flux in (or out)...”

Smith found that the resultant life time (the diagonal element of the life time matrix), when applied to the one-dimensional case and when properly averaged to smear out an oscillating term, reproduces the phase time as in Eqn.(2.1), thereby shedding new
light on the physical meaning of phase time. Hence the phase time is often called as ‘Eisenbud-Wigner-Smith time’ $\tau_{WES}$ (Wigner-Smith time or Bohm-Wigner time), especially in the recent literature. Incidentally, the above idea on which Smith’s collision life time is based is essentially the same as the one on which a tunnelling time known as the dwell time is based. Hence Smith’s collision life time is often regarded as a root of dwell time.

In all the above works wherein the projectile is considered as a wave-packet, the peak of the wave-packet is well-defined i.e. the wave-packet is localised sharply around a given wavenumber $k$ such that momentum $p = \hbar k$ and the complex transmission amplitude is given by $T(k) = |T(k)|e^{i\theta_k}$. If we consider a rectangular opaque barrier of width $a$, this would yield a transmission group delay as,

$$\tau_{WES} = \frac{\hbar d\theta}{dE_n} \approx \frac{2}{v\kappa},$$

where $v = \hbar k/m$ and $1/\kappa = \hbar/\sqrt{2m(V - E_n)}$ is the penetration depth. This was met with strong objections [53–55] as the wave-packet could be distorted considerably after its transmission through the barrier, which was clearly shown with a simple example in [56]. Alternatively, methods employing the centroid or centre of gravity of the wavepacket were formulated to calculate time delays [57,58]. In addition to the wavepacket distortion, the delay in Eqn.(2.1) is independent of the barrier-width when it is very large and hence for such barriers, this can lead to superluminal speeds, namely the Hartman effect [59]. This is due to the difference in the transmission of the faster component of the wavepackets when compared to its slower counterparts. It can also at times lead to negative group velocities, that seem to apparently violate causality. Experiments related to these superluminal speeds can be found in [60,61].

### 2.3.2 Tunnelling times using clocks

In one of his most influential papers on tunnelling time [53], Büttiker differentiates the subtlety in asking the question “How long does a particle spend in the classically forbidden region?” from that of “How long does it take a particle to tunnel through the barrier?” He states that:

... An approach given by Smith, and advanced by others yields a time
as the ratio of the number of particles under the barrier to incident flux... This method does not distinguish between particles which at the end of their stay in the forbidden region have been reflected, and those that were transmitted. This time is the average dwell time of a particle in the barrier, and is not the traversal time, if most particles are reflected...

This formed the motivation for a second class of tunnelling times defined as traversal time. This involves an extra degree of freedom associated to the barrier, which can be used as a clock to measure the amount of time the particle interacted with it. This set of times are famous largely due to a series of publications by Büttiker and later with Landauer [53–55,62,63].

Büttiker-Landauer time $\tau_{BL}$

Here the particles with energy $E_n$ and mass $m$ are incident upon a rectangular barrier of width $d$ and height $V_0$ accompanied by a small oscillation in its height i.e. $V(x,t) = V_0(x) + V_1(x)\cos(\omega t)$ (see Fig.2.2). Considering the frequency of the oscillation to be lower than the interaction time of the particle, it tunnels elastically through the static barrier. At high frequencies the particle sees a time-varying potential and tunnels through it inelastically either by absorbing or giving a quanta of energy $\hbar\omega$. The frequency of this oscillation $\omega$ is tuned to a wide range such that a crossover is achieved between the two behaviours. When the frequency resonates with inverse of interaction time we have $\omega\tau_{BL} = 1$. They have shown that the traversal time i.e. the interaction time of the particle of mass $m$ with the barrier (for $E_n < V_0$) is given by $\tau_{BL} = md/\hbar\kappa$ for rectangular barriers, and by Eqn.(2.2) for barriers of a more general shape that allows WentzelKramersBrillouin (WKB) approximation.

$$\tau_{BL} = \int_{-d/2}^{d/2} \sqrt{\frac{m}{2}}\sqrt{\frac{1}{V_0(x) - E_n}}dx.$$  (2.2)

Experimentally, the traversal time can be measured by observing the crossover frequency in the energy spectrum of the transmitted particles. At low frequencies the transmission energy sidebands (considering only to the first order) of $E_n \pm \hbar\omega$ appear equal in their magnitude. However at the higher frequencies they are asymmetric due to the enhanced transmission probabilities for the higher energy side band.
gain a quanta) than the lower ones (that lose a quanta). If $T$ is the transmission probability of the static barrier, the transmission probabilities of the sidebands $T_{\pm}$ are,

$$T_{\pm} = \left(\frac{V_1}{2\hbar \omega}\right)^2 (e^{\pm \omega \tau} - 1)^2 T.$$  \hspace{1cm} (2.3)

These are then used to yield a simple relation for the interaction time as,

$$\frac{(T_+ - T_-)}{(T_+ + T_-)} = \tanh(\omega \tau_{BL}).$$ \hspace{1cm} (2.4)

Considering the special case of opaque barriers, the WKB approximation allows the formulation to extend beyond rectangular barriers and a general formula [63] was defined subsequently as

$$\tau_{BL} = -\hbar \frac{\partial \ln |T|}{\partial V}.$$ \hspace{1cm} (2.5)

A good overview on the experiments performed in attempts to determine the above discussed traversal times can be found in [64] (and references therein). To cite a few that proposed and reported the observation of crossovers as putforth by [53] are [65–67]. In [65], macroscopic tunnelling rate was measured using Josephson junctions. Josephson junction is a quantum mechanical device wherein a resistor is sandwiched between two superconductors. The resistor acts like a barrier for the cooper pairs of electrons to tunnel through it (with propagation velocity $v$), creating a
current that is carried along a closed path of length $l$, known as the transmission line. Considering the traversal time is longer than the delay through the transmission line $2l/v$, the tunnelled waves can interfere among themselves back and forth, decreasing the overall tunnelling rate. On the other hand, if the traversal time is much smaller than the delay introduced due to increased length, they can no longer interfere. A crossover was indeed observed as predicted by the time modulated barrier case [53] while changing the length from which traversal times were calculated. An interesting set of experiments were performed by [67] in which quantum heterostructure was used to fabricate rectangular barriers of various thickness and heights that change dynamically as the electron traverses through it. They also revealed a crossover as predicted in the case of time-modulated barrier systems.

The I-V characteristic features of a scanning tunnelling microscope (STM) were measured to calculate traversal times [66] while a polarized beam is incident on its junction. When a linear polarized light is focussed in a way that the electric field vector is aligned along the tip of the axis, a bias is formed inducing a current back and forth following the laser field. This occurs even with no external voltage being applied across it. Given the rectification property of the STM, it should generate a DC current if the laser frequency is small compared to the transit time of electrons and vice versa. They observed the electron transit time to be $\sim 1.8$ fsec that agrees qualitatively with the $\tau_{BL}$. However, interpretation of such results using 1D models are not so easy as described above, due to a complicated geometry involved in the STM set-up. This, in addition with other critical comments was later pointed out in [68] (see pp.146-147).

A close variant of such a scenario of oscillating barrier is also found in relation to optical tunnelling of an electron under the influence of strong external fields (see Sec.1.2.2). In the limit of $\gamma \ll 1$ from Eqn.1.5, the suppressed Coulomb potential oscillates adiabatically with the external field, changing the barrier height and width. Keldysh parameter is then interpreted as the ratio of the characteristic tunnelling time, defined as the Keldysh time ($\tau_{kel}$), to the laser period. However, we restrict the discussion of tunnelling times and its measurements with regards to strong-field physics to Chapter 3.
Figure 2.3: A spin-1/2 particle (spin polarised in Y direction) with energy $E_n$ is incident on a rectangular barrier of width $d$ and height $V$. The transmitted particles that undergo Larmor precession by an angle $\theta$ gives the $\tau_{LM}$. Alternatively, the barrier height is modulated by Zeeman splitting $\pm \hbar \omega_L/2$ ($\omega_L$ is the Larmor frequency) under the influence of magnetic field $B\hat{z}$ confined within the barrier. The sidebands formed in the energy spectrum allows one to calculate the traversal time $\tau_B = \sqrt{\tau_{BL}^2 + \tau_{LM}^2}$.

Larmor time

An alternative clock invoking an interaction between the spin of the particle and the barrier confined by a magnetic field was proposed by Baz’ [69] and Rybachenko [70]. They considered spin-1/2 particles of energy $E$ that are spin polarized in the Y direction ($\langle S_x \rangle = \langle S_z \rangle = 0, \langle S_y \rangle = \hbar/2$) which were then influenced by the magnetic field $\vec{B} = B\Theta(z)\Theta(d - z)\hat{x}$ confined within the barrier of width, $d$ and height, $V$. By comparing the spin orientation of transmitted particles due to Larmor precession relative to the incident particles, the tunnelling time could be computed. This is termed as Larmor time in the literature and is expressed as the (barrier) potential derivative of the phase acquired by the transmitted particles,

$$\tau_{LM} = -\hbar \frac{\partial \theta}{\partial V}. \quad (2.6)$$

By only considering the $S_y$ components, Rybachenko found that $\tau_{LM}$ to be independent of the barrier width. However Büttiker [62] realized that the Zeeman splitting of the $S_x$ component could lead to $\langle S_x \rangle = \pm \hbar/2$, making the effective barrier height as $\mp \hbar \omega_L/2$, respectively where $\omega_L$ is the Larmor frequency. This could lead to a preferential tunnelling for particles with $\langle S_x \rangle = +\hbar/2$. This allowed him to
reinterpret the problem using the approach of modulated barrier case and derived three characteristic times that explains the particle’s interaction with the barrier: dwell time\(^1\), traversal time and reflection time. Dwell time measures the average time that the particle interacts with the barrier irrespective of its final state and was defined as,

\[
\tau_d = \frac{1}{v} \int_0^d |\psi(z)|^2 \, dz,
\]

with \(v\) being the velocity of the incident particle and \(\psi(x)\) being the stationary wavefunction inside the forbidden region \(0 < x < d\). Traversal/reflection times (\(\tau_T/\tau_R\)) were defined as the transmitted/reflected particle’s interaction time with the barrier and were expressed using the transmittance/reflectance coefficients. Now, by considering the parallel component of spin \(S_x\), the traversal time was shown to vary linearly according to the barrier width, unlike what Ryabachenko calculated. This traversal time is sometimes also called as Büttiker time \([71]\) \(\tau_B\) and shall not be confused with the Büttiker-Landauer time \(\tau_{BL}\). In fact for the rectangular barriers the traversal time was shown to be \(\tau_B = \sqrt{\tau_{BL}^2 + \tau_{LM}^2}\) \([72]\). In the special case of opaque barriers the phase becomes insensitive to the barrier, therefore yielding us \(\tau_B = \tau_{BL}\) as in Eqn.(2.5).

Although experimentally realising Larmor clocks as suggested above is challenging, there were experimental studies done measuring the effect of weak transverse magnetic fields on the traversal times using heterostructures \([74,75]\). Interestingly, an optical equivalent of electron is used to measure Larmor times \([73]\). The electron spin is replaced with the photon polarisation and the uniform magnetic field by a birefringent liquid crystal. The stokes parameter vector on the Poincaré sphere is measured to determine the precession caused by the anisotropy of the liquid crystal’s refractive index. The optical equivalent of tunnelling scenario is shown in Fig.2.4. The light is incident on the first prism of refractive index \(n_H\) with an angle beyond the critical angle. The evanescent field is frustrated total internal reflected (FTIR) \([76]\) through the liquid crystal of relatively lower refractive index \(n_L\). The phenomenon of FTIR is optically equivalent to quantum tunnelling. By varying the wavelength of the light they could control the effective barrier thickness. However due to a strong

\(^1\)This must not be confused with the average dwell time that Smith introduced. Unless otherwise stated, dwell time in the literature of tunnelling times refers to the definition given by Büttiker.
anisotropy in the refractive index, the results could not determine traversal times unambiguously.

It is noteworthy to mention at this point, that the words ‘time-delays’, ‘dwell time’, ‘traversal time’, ‘Büttiker-Landauer time’ are not strictly adhered to their definitions. They were redefined/reused/generalised in many different ways in the course of history and hence should be contextualised when read or used. For example ‘Büttiker [53] called $\tau_{BL}$ as the traversal time but in [63] $\tau_B = \sqrt{\tau_{BL}^2 + \tau_{LM}^2}$ was called the traversal time, which was later called as Büttiker-Landauer time by others [77].

As stated before, for the special case of opaque rectangular barriers $\tau_{LM} \approx 0$ making $\tau_B = \tau_{BL}$. Although in some recent literature, for some historical reasons, $\tau_{BL}$ as in Eqn.(2.5) was called as the Büttiker-Landauer time, there exists a consensus among the tunnelling physics community that $\tau_B$ be defined as the Büttiker-Landauer time in its broadest sense. Similarly the concept of time-delay was also understood and used in different contexts [48, 57, 78]. We have already seen two different ways of defining ‘dwell time’ and we are yet to introduce its usage from a classification point of view in the next section. Also ‘sojourn time’ is often used synonymously in the literature in place of dwell time.
2.3.3 Complex times

Pollak-Miller time

Extrapolating the classical problems to the realm of quantum mechanics often can lead to complex quantities. This is also true while considering classical collisional theories in quantum mechanical context. Pollak and Miller [79] took such an approach of considering the collisional time to be a time average of a flux-flux correlation function. The idea was partly motivated due to the success of the kinetic definition by Smith [52] being equivalent to the phase time-delays. If tunnelling delays are regarded as the excess time taken by the wavepacket colliding with a non-zero potential, Smith showed that it is equivalent of an average time spent by the incoming flux of particles spent in the interaction region. Hence from a kinetic point of view, considering both the incoming flux of particles and particles in the interaction region, the delays would correspond to the ratio of these two numbers. This had led to the definition of Smith’s dwell time. Following this prescription, Pollak and Miller arrived at complex traversal times and they called it the _quantal imaginary time_ [79] in the context of scattering theory. Later in [80] it was argued that the real time of their complex traversal time gives the Smith time, while the imaginary part of it gives the true interaction time in the tunnelling picture. This true interaction time is now known as the _Pollack-Miller time_,

\[ \tau_{PM} = \hbar \frac{\partial \ln |T|}{\partial E_n}. \] (2.8)

2.3.4 Feynman path-integral technique and tunnelling times

In 1948 [81], Feynman gave a new and yet an equivalent description for the quantum mechanical formulation of calculating amplitudes and probabilities by generalising the action principle. In his formulation, amplitudes are calculated by assigning a sum of infinite classical trajectories that a quantum particle can possibly take in space and time. This description was initially put to use in the tunnelling context by Sokolovski and Baskin [82]. They provided general expression for traversal times and constructed complex time parameters that can relate to the already existing traversal times mentioned above in the form of \( \tau_{LM} - i \tau_{BL} \). The complex time relating as \( \tau_{EWS} - i \tau_{PM} \) was already shown by [72] in their attempt to extend
Büttiker-Landauer times to arbitrary barriers. These 2 complex traversal times in the combinations as mentioned above were derived in a unified manner using GellMann-Hartle decoherence functionals [83] with the path integral approach [84].

To briefly summarise the results of [84], the quantity of interest was the sum of all those times during which a Feynman path \( x(t) \) was inside the barrier as shown in the left of Fig. 2.5. Alternatively, one can also adhere to a definition of the time difference between the first instant of time a Feynman path entered the barrier to the last instant when it left the barrier (right side of Fig. 2.5). These different descriptions led to two different probability distributions \( f(\tau) \). Upon calculating the quasi average of these two different distributions, led to two classifications of the traversal times namely dwell time/resident time, \( \mathcal{T}_d \) and passage time, \( \mathcal{T}_p \), respectively. Incidentally, these were related to the well known tunnelling times as:

\[
\mathcal{T}_d = \tau_{LM} - i\tau_{BL}, \quad \mathcal{T}_p = \tau_{WES} - i\tau_{PM} - \hbar/2E_n. \tag{2.9}
\]

Considering the transmission coefficient to be \( T = |T|e^{i\theta} \), the tunnelling times \( \tau_{BL}^2 \), \( \tau_{LM} \) derived using the potential derivatives of transmission coefficient \( (\partial \ln T/\partial V) \) were understood as the dwell time (see Eqn.(2.5) and Eqn.(2.6)) and the energy derivative of transmission coefficient \( (\partial \ln T/\partial E) \) were understood to be the passage time (see Eqn.(2.1) and Eqn.(2.8)). These classifications are entirely at the level of Feynman paths and can be physically interpreted as the time measured by barrier (for dwell times) and traversing particle (for passage times) [84].

### 2.4 Summary

A brief overview of tunnelling times and its history is presented, with some relevant experimental works related to them. Except for some notable and frequently cited works, we have not mentioned many other important works, which we would direct the reader to find in [77,85–88] and references therein. It is clear from the above discussed literature, that the definition and interpretation of tunnelling time is not

\[\text{In [84], the } \tau_{BL} = -\hbar\partial \ln |T|/\partial V \text{ was called a tunnelling time of resident (or dwell) time type, in the sense of being obtained from the segments of Feynman paths that lie only inside the barrier region. This does not mean that the Büttiker-Landauer time is the same as the dwell time } \tau_d \text{ which Buttiker introduced in [62] as seen in Eqn.(2.7).}\]
unique. The usage of various names itself poses an initial confusion for the reader to understand tunnelling times. The path integral approach had helped to some extent in generalising tunnelling times by deriving the well known quantities not only in a unified manner but also devoid of any specific physical model.

In spite of various experiments been performed in an attempt to validate different models of the tunnelling times, it is still a matter of debate among the physics community. For example, soon after the optical Larmor clock experiment [73] as mentioned above in Sec.2.3.2, Balcou and Deutriaux [89] successfully performed a similar experiment using FTIR. In their attempt to measure the traversal times, they ended up measuring two traversal times simultaneously – phase time-delays and the Larmor time. Interestingly, both of these observations agree with their respective theories, however which one to be called ”the real tunnelling time” is an open question. On the same note, though crossovers were observed in the experiments [65–67] discussed in Sec.2.3.2, no definite conclusion were drawn in invalidating other available tunnelling theories over Büttiker-Landauer time [88] (see p. 223), [63] (see p. 311) and [71] (see p. 227). At this point, it is worthwhile to end the discussion on tunnelling time theories with what Landauer and Martin stated in [88] that would summarise the ongoing debate regarding tunnelling times:

...’Do we need to bother about traversal time; is it an indispensable concept’? Of course it is not. Physics is full of alternative viewpoints...Traversal time, like the uncertainty principle, is a useful con-
ceptual tool. It does not permit us to find answers, unavailable in other ways. The concept can be avoided if it is not to your taste. There is no copyright on the expressions traversal time and tunnelling time; each author can choose an interpretation... We can only ask if this is a fruitful view, and we can ask if it is relatable to experiment... Attitudes toward traversal time are, as in any area of uncertainty, often tied to a particular background...
This chapter introduces the theory of optical tunnelling and tunnelling time in the context of strong-field physics. As a quick recap, in strong-field regime the interaction of the laser pulse with an atom depends highly non-linearly on the instantaneous electric field strength of the pulse. In the case of the commonly used carrier wavelength of 800 nm one oscillation takes 2.7 fs, so that temporal dynamics proceed on a sub-femtosecond timescale. Under strong few-cycle short pulse laser field interaction with atoms, the bounded electron can ionize from the atom by tunnelling through the potential barrier. Under such conditions, a technique known as attosecond angular streaking (AAS) technique [90] allows one to probe the ionization dynamics in attosecond timescales by using femtosecond pulses. AAS technique maps time to the angle of the photo-electron\(^1\) momentum distribution (MD) giving information about the tunnelling dynamics.

The first section provides a brief introduction to the simpleman’s model for the tunnel ionisation. It is a semi-classical model based on which the attoclock technique was conceived. The second section discusses the AAS technique and ‘tunnelling delay’ with their importance to the study of laser-matter interaction. We then proceed to the discussion of previous experimental and theoretical work with regard to various targets on which the technique (experimental and numerical) was performed. There is also a brief review on various interpretations that these experiments have led to and its understanding on how it may help us to infer the tunnelling times. The chapter finally ends with a motivation for the necessity to perform this experiment with atomic hydrogen.

\(^1\)Please note that ‘photo-electron’ in the thesis corresponds to an electron ionised through strong-field ionisation and does not correspond to an electron ionised due to a photon unless it is specified.


3.1 Simpleman’s model and tunnelling times

At present, it is difficult to understand completely the process of tunnel ionisation due to the dynamics involved and the theoretical limitation which requires one to solve the TDSE with all the interactions included. Nevertheless, great insights were possible in understanding strong field phenomena due to the semiclassical model that is also known as ‘Simpleman’s model’ [91–93]. In this model, the process of tunnelling is considered as the first step. Second step is the treatment of the unbound electron that appears at the tunnel exit, interacting with the field as a free particle. In some instances, this step is followed by a third step where the electron is accelerated back towards the parent-ion and can rescatter. During these last two steps, the external field strength is considerably strong and hence the residual ion-electron interaction is neglected. This is known as SFA [19].

The first step of tunnel ionisation would obviously make one ask the pertinent question of ‘How long does it take the electron to tunnel through the barrier?’ Here, the scenario is different from all the previous tunnelling models we saw in Chapter 1 as the projectile is not a free particle initially. The quantum particle is tunnelling from a bound state to a continuum state. However, such problems were studied using the Wigner-Eisendbud-Smith delays in the context of photo-ionisation by attosecond pulses [94–97]. These time-delays are well modelled using phase-times as discussed in Chapter 1, since the outgoing electron wavepacket interacts with the atomic potential for a very brief time (in attosecond timescales) giving it a relative phase shift. In the case of single-photon ionisation, the outgoing wavepacket has a well-defined peak while the tunnelled wavepacket doesn’t, which makes it untenable to use phase-times for calculating tunnelling delays. As we have seen in the previous chapter that different tunnelling times can be derived from Feynman path-integral approach. Such works had been undertaken in the context of tunnel ionisation in [98] which shall be discussed later in Sec.3.2.1. Before that, we shall restrict ourselves to the discussion of a semi-classical description that plays an important role in providing us with an intuitive description of tunnelling.

Semi-classically, the external field $\vec{E}$ suppresses the Coulomb field creating an effective potential $V_{\text{eff}} = -Z_{\text{eff}}/x - Ex$ as shown with a red thick line in Fig.3.1.
Figure 3.1: Potential curves (in 1-D for simplicity in atomic units) for an atom in the presence of an external field $\vec{E}$. The blue dot-dashed line represents the unperturbed Coulomb field of charge $Z_{\text{eff}}$ while the red thick line represents the suppressed Coulomb potential, the effective potential $V_{\text{eff}}$. Electron in its bound state of energy $-I_p$ tunnels through the barrier and exits at point $d$, known as the classical tunnel exit. Height of the barrier is given by $I_p - V_{\text{eff}}(x_m) = I_p - 2\sqrt{Z_{\text{eff}}E}$ and $x_m = \sqrt{Z_{\text{eff}}/E}$ is the extremal point of $V_{\text{eff}}$. $d_{\pm}$ corresponds to the points $V_{\text{eff}} = -I_p$, the two end points of the barrier. The figure is adapted from [99].

During the process of tunnelling the electron traverse through the barrier of length $d$ (without considering the distortion caused by the Coulomb barrier) with an average velocity of $v_{\text{avg}}$. Hence the time a classical electron takes to tunnel through the barrier can be expressed as $\tau_{\text{kel}} = d/v_{\text{avg}}$, known as the Keldysh time. $d$ is known as the classical exit point and can be derived by using the information of the strength of external field $E$, that forms the slope along the points origin and $(d, -I_p)$. Thus we have $d = I_p/E$. With the initial energy of the electron to be $1/2v_i^2 = -I_p$, the electron looses all its kinetic energy in overcoming the barrier leading to a final velocity $v_f$ at the tunnel exit as zero, hence $v_{\text{avg}} = \frac{v_f - v_i}{2} = i\sqrt{I_p/2}$. The velocity is imaginary (so is the time) as the electron is traversing under the barrier. By using the above expressions and Eqn.(1.5)-(1.6) the Keldysh time is:

$$\tau_{\text{kel}} = d/v_{\text{avg}} = \frac{i\sqrt{2I_p/E}}{E} = i\gamma/\omega_0.$$  \hfill (3.1)
Therefore $\gamma$, known as the adiabaticity parameter, can now be thought as the ratio of tunnelling time to that of the laser period. In the tunnelling regime, the time period of each laser cycle is larger than the tunnelling time and hence the atom can follow the external field adiabatically with electron tunnelling through an oscillating barrier, as in the case of the Büttiker-Landauer tunnelling time, $\tau_{BL}$. Hence, the Keldysh time $\tau_{kel}$ is a close cousin of the $\tau_{BL}$ in the strong field regime. Interestingly, if the conventional definition of momentum ($\sqrt{2m(E_n - V)}$) is inserted into the Eqn.(2.2), we can see that $\tau_{BL}$ is also imaginary. However Büttiker-Landauer argued that the tunnelling time cannot be imaginary and hence one should consider the imaginary part of momentum or $\tau_{BL}$ for the real traversal time [53].

Recently, tunnelling times in strong field processes were calculated [100] using the time-energy uncertainty relation (TEUR) as prescribed by Mandelstam-Tamm [101]. These were shown to be numerically equal to the value of Keldysh times [102]. Borrowing the ideas of TEUR and considering the process to be similar to a Bohr-Einstein weighing photon-box [103, 104], a symmetric tunnelling time $\tau_{sym}$ was derived [99]. Unlike the semi-classical case of considering the barrier length to be $d$, the author considers $d_-(d_+)$ as the barrier entrance (exit) point (see Fig.(3.1)). These can be calculated by simply solving for $x$ from $V_{eff}(x) = -I_p$ [99]:

$$d_+ = I_p \pm \sqrt{\frac{I_p^2 - 4Ze_{eff}E}{2E}}.$$  

Here the $\tau_{sym}$ is defined as the sum of (i) the time it requires for the electron to interact with the external field to enter the barrier at the point $d_-$ and (ii) the time it takes to travel across the barrier and reach point $d_+$, from which it escapes to the continuum. This was shown to be inversely proportional to the field strength and is given by:

$$\tau_{sym} = \frac{I_p}{4Ze_{eff}E}.$$  

It is important to note that both $\tau_{kel}$ in Eqn.(3.1) and $\tau_{sym}$ in Eqn.(3.3) are

---

2This is a gedanken experiment where a photon placed in a box with a shutter, is allowed to escape as the shutter opens for a brief interval of time $\Delta t$. Bohr showed [103] that measuring the relative change in the mass and thereby energy (since $E_n = mc^2$) of the box within an error of $\Delta E_n$ leads to the TEUR such that $\Delta t\Delta E_n \geq \hbar/2$. $\Delta t$ can then be interpreted as the passage time for the photon to escape. An alternate explanation was given by Busch [104], where by measuring the relative energy of the photon (before and after the shutter is open) with an $\Delta E_n$ error could be used to infer $\Delta t$ using TEUR.
inversely related to the field strength. This is due to the reduction in the area of
the barrier as external field grows stronger. We have already calculated the barrier
width to be \( d = \frac{I_p}{E} \). The height of the barrier \( h \) can be calculated by finding the
maxima of the potential curve \( \max(V_{\text{eff}}(x)) = V_{\text{eff}}(x_m) \) (see Fig.3.1), where \( x_m \) is
the extremal point such that,

\[
\left. \frac{\partial V_{\text{eff}}}{\partial x} \right|_{x=x_m} = 0 \quad \text{and} \quad \left. \frac{\partial^2 V_{\text{eff}}}{\partial x^2} \right|_{x=x_m} < 0,
\]

\( \Rightarrow \quad x_m = \sqrt{\frac{Z_{\text{eff}}}{E}}, \quad \tag{3.4a} \)

\[
\cdots h = I_p - V_{\text{eff}}(x_m) = I_p - 2\sqrt{\frac{Z_{\text{eff}}}{E}} E. \quad \tag{3.4c}
\]

It shall be now be clear that the barrier height \( h \) and the width \( d \) both decrease
together with the increasing field. Hence by considering an electron as a particle
traversing barrier, one shall expect to see a trend of decreasing tunnelling times as a
function of increasing field strength.

All the above approaches of tunnelling times were purely from a theoretical
perspective and described using a semi-classical model for a static external strong
field. But in the physical picture which we are interested, the strong field interaction
is produced using ultrashort laser pulses, wherein the external field is continuously
changing. Hence it is important for one to devise a mechanism experimentally, by
which one can measure these tunnelling times. This is now possible using the AAS
technique [90] discussed in the following section.

### 3.2 Attosecond angular streaking

Complying to the simpleman’s model and considering the adiabatic formula of ADK
as given in Eqn.(1.10), one can estimate the ionisation rate as a function of external
field. This would yield us the ionisation rate curve that peaks with the peak electric
field. Nonetheless, a finite time would imply a delay in the release of a bound electron
into the continuum, which is when the ionisation event is said to be finished. Hence,
a finite tunnelling time would imply a finite delay in the peak of ionisation rate as
compared to the peak field that is liberating the bound electron. Unfortunately,
the tunnelling time estimates are so short that they are around few tens to 100s of
attoseconds and also the ionisation rate is not directly accessible to experimentalists. Moreover, a reversal in the direction of electric field can lead to re-scattering events perturbing the trajectories of the direct tunnelled electrons that we are interested in. Although the probability of rescattering events is quite low, segregating these events from the direct electrons in the signal is a challenging task. Therefore, it is required of us to employ a clock that can measure these tunnelling delays precisely within 10s of attoseconds timescales and avoid the re-scattering events. The technique of AAS or ‘attoclock’, that was conceived based on the semi-classical model [105] offers precisely this. Tunnelling delays are defined and measured by using the time difference between the peak of the ionising field and the instant when the electron appears in the continuum.

AAS uses few-cycle near-circularly polarised pulses as a clock to measure tunnelling delays. The field of such a pulse with a Gaussian envelope $G(t)$ is (see Fig. (3.2)):

$$\vec{E}(t) = G(t) [E_x \sin(\omega t)\hat{x} + E_y \cos(\omega t)\hat{y}] .$$  

(3.5)
This has three advantages; firstly, the circular polarised pulses prohibit recombination or re-scattering of electron into the ion core. Secondly, a few-cycle pulse is a short pulse that comprise of not more than 1-1.5 optical cycles around the peak of the pulse. This ensures that the field varies very quickly such that the maximum ionisation probability occurs only at one point, i.e. at the peak field. Third and most important thing is that it enables electric field vector at an instant in time \( \vec{E}(t) \) be mapped to an angle in space and can be measured simply using polarisation optics. Due to adiabaticity, the electron shall start tunnelling at the time the field reaches its maximum value. This forms the first step of the AAS technique. The tunnelled electron then is streaked upon the force acted by the electric field post its appearance at the tunnel exit at time \( t_0 \), taking its final momentum to a value \( p_f \):

\[
p_f = \int_{t_0}^{\infty} \vec{E}(t) dt. \tag{3.6}
\]

Hence the final momentum is numerically equal to the field’s vector potential at the instant of its ionisation. Since the vector potential changes its direction constantly in the polarisation plane with a rate \( \omega \), the angular frequency, it sweeps every degree for \( \frac{\pi}{\omega \times 180} \) seconds. For a typical 800 nm central wavelength pulses, the relation goes as \( 1^\circ \approx 7.4 \text{ as} \). Assuming no tunnelling delay and SFA the electron appears at \( t_0 = t_{\text{peak}} \) in the continuum, where \( t_{\text{peak}} \) corresponds to the time when electric field reaches its peak value, \( E_0 \). When seen in the polarisation plane (see Fig.3.2), this would imply that the electron flies in a perpendicular direction to that of \( E_0 \). We assign this shift of \( 90^\circ \) relative to the direction of \( E_0 \) as \( \theta_{\text{streak}} \). Any amount of finite tunnelling delay \( t_i \) would change the initial condition for streaking thereby leading to an additional offset, \( \theta_{\text{delay}} \).

### 3.2.1 A review of AAS experiments

It has been a decade since the first attoclock experiment [90] was performed. Yet, the controversy and debate surrounding the tunnelling times in the context of strong field ionisation has not subsided. Tunnelling delay times were first measured using helium [90,106] as the gas target. The observable that shall be measured is the angular offset present in the asymptotic momentum of the streaked ions/electrons, in the
polarisation plane. Cold target recoil ion momentum spectrometer (COLTRIMS) [107] was used to measure the asymptotic momentum $p_f$. A detailed description of the COLTRIMS is provided in Chapter 3. The angular offsets were calculated by finding the difference between the MDs using semi-classical simulations assuming adiabaticity and the experimentally measured MDs. The experiment was performed in an intensity range of $2.3 \times 10^{14}$ W/cm$^2$ to $3.3 \times 10^{14}$ W/cm$^2$, corresponding to $\gamma = 1.45$ to 1.17. It was found that the tunnelling delays were zero within an uncertainty of 12 asec against what $\tau_{BL}$ or $\tau_{kel}$ would predict which is $\sim 500$ attoseconds. Thus, the authors concluded that there were no signs of real tunnelling delays. Although the authors included the contributions of possible parent ion-electron interaction during the streaking process in their semi-classical simulations that showed to be non-zero but constant across the intensity range, it was soon followed with a detailed description of a semi-classical model [105] that did not include any Coulomb contributions which also interestingly explained the experimental results successfully.

Their semi-classical model uses the ADK formula in combination with the post-tunnelling classical trajectories of continuum electron. But such a theory had not gone uncontested. Although this theory would come handy for experimentalists to qualitatively (and quantitatively to some extent) gauge their results instead of relying on more computationally challenging TDSE simulations, it is prone to many limitations. To begin with, the authors themselves mentioned a limitation of such a theory that lies in a scenario where the ground state depletes at higher intensities. Later [108] pointed out that, in addition to the depletion effects, it is possible to ionise electrons before the field reaches $E_{peak}$ at higher intensities. This time was calculated to be more than the typical tunnelling delays. Using 3D-TDSE codes, [109] showed that counter-intuitive angular shifts can be observed in argon, due to the effect of the ever existing Coulomb field. They also showed that the theories like ADK or SFA can be misleading in predicting the most dominant direction of the ionised electrons. All these posed a challenge in interpreting the angular offsets in terms of tunnelling times. In fact, this was acknowledged in a successive experiment carried out on argon and helium again [110, 111], albeit in a larger intensity range ($\sim 3 - 1.5 \times 10^{14}$ W/cm$^2$) with 7 fs pulses:

"...This Coulomb correction is especially sensitive to the ion-electron
Figure 3.3: (Left) Various known tunnelling times in comparison to the time mapped from measured angular offsets after subtracting the Coulomb effects calculated using TIPIS and classical trajectory Monte-Carlo models. Larmor times and the curve ‘FPI’ are shown to be in good agreement with the experiment. The curve ‘FPI’ is plotted by choosing the $\max(f(\tau))$ calculated using Feynman path integral approach. (Right) A probability distribution of tunnelling time $f(\tau)$ calculated using path integral approach for a triangular barrier corresponding to the intensity $1.625 \times 10^{14} \text{ W/cm}^2$. The FWHM of the peak is 80 as and the oscillatory nature of the graph is due to the interferences of multiple paths in space-time. The figure is adopted from [98].

attraction at the beginning of the electron trajectory. In general however this angular offset $\theta$ is much more complicated and not fully explored and understood to date. ...” [110]

It was noted that to provide an appropriate semi-classical theory it’s important to know the initial conditions of the electron emerging into continuum. This depends strongly on the tunnelling geometry. To this end, a new semi-classical model was introduced, analysing the system in parabolic coordinates, that includes the Stark effects, namely, tunnel ionization in parabolic coordinates with induced dipole and Stark shift (TIPIS) model. This model in conjunction with the AAS technique also concluded that there were no real tunnelling delays, but demonstrated the importance of how electron-electron correlations in the atom could possibly complicate the trajectories and thereby the interpretation of angular offsets.

The two sets of experiments with helium only went on to show zero tunnelling delays, partly because the latter one was done at the higher end of the intensity range that enters the over-the-barrier ionisation regime. The claim for a real tunnelling time in the context of strong-field ionisation was only reported a year later [98,112], when
the experiment was transferred to a velocity-map imaging (VMI) apparatus [113], due to its high detection efficiency yielding better count rates even at lower intensities. This third set of experiments probed tunnelling delays in wide range of intensities (0.73-7.5×10^{14} W/cm^2) varying the barrier size by almost 3 times. The angular offsets measured were non-zero after considering the Coulomb corrections obtained from the TIPIS model and were attributed to real tunnelling times.

It can be seen that from Fig.3.3, the experimental observation is compared with the known tunnelling times $\tau_{BL}$, $\tau_{PM}$, $\tau_{LM}$ and $\tau_{WES}$ as given by their definitions mentioned in Chapter 1. The tunnelling barrier is modelled as a triangle and the Feynman path integral method was employed to calculate the distribution function of tunnelling time $f(\tau)$. As described in Chapter 1, the known tunnelling times could be derived by following different definitions that give rise to $f(\tau)$. Nevertheless, ‘which one should be considered as the correct one?’ was an open question. The authors reported [98,114] that the times calculated from the observed non-zero offsets were in good agreement with one of those times – the Larmor time $\tau_{LM}$. In addition to this, they have also showed that the peak value of $f(\tau)$ predicts the tunnelling time better.

The procedure of Feynman-path integral is appealing as, unlike the semi-classical models, it treats the whole problem quantum mechanically and is equivalent to considering the electron as a wavepacket. But it should be mentioned that the path integral approach goes to prove that the tunnelling time is not a deterministic quantity but a probability distribution, which would only further complicate the interpretation of the observed angular offsets to tunnelling time. On the contrary, recent work [99] using the symmetric time $\tau_{sym}$ definition while treating the electron as a particle during tunnelling process together with the TEUR, claimed to be in good agreement with the attoclock experimental data. A detailed review of this work and how its interpretation of tunnelling time is different from path-integral approach can be found in [115].

Despite all this, the debate continued in the strong-field community on the grounds that the angular offsets could not be reproduced by any of the known theoretical models. This is in fact a serious concern as the calculations of angular offsets, from which time is deduced, rely on theoretical models used. This disagreement could
be assigned to the non-adiabatic nature of interaction, which shall be taken care of in the process of calibrating intensities and ionisation rates and/or the failure of modelling helium within the SAE approximation. The justification for using adiabatic models was argued in [116] by showing that non-adiabatic nature of interaction could not predict the qualitative trend as observed in the experiment. This argument was soon disputed by a paper that showed the contrary [117] and had put the assumptions of the semiclassical model TIPIS to question, challenging its validity. The argument of electron-electron correlations was put to rest [118] by a 3D-TDSE code developed based on the hybrid anti-symmetrised coupled channels method [24], which can completely solve helium interacting with an elliptically polarised light. These results also could not reproduce the measured offsets in the attoclock setting for helium. Currently, the observations remain in disagreement with the state-of-the-art strong-field models, leaving the question of tunnelling time in strong-field physics unanswered.

Recently, an attoclock experiment performed on a mixture of krypton and argon gases claimed to have measured tunnelling times around $\sim 100$ as [119], by measuring relative offsets between the two species. The authors argue that by making use of relative offsets, they could cancel out the contributions of the Coulomb attraction by the parent ion. They used a higher wavelength laser pulses to satisfy the condition $\gamma < 1$, so as to overcome the complications due to non-adiabaticity. Wigner delays were used to find the most dominant quantum path that exit the tunnel at point $x_{exit}$ at time $t_{exit}$ with longitudinal momentum $p_{exit}$. These are then used as the initial conditions for the classically propagating electron in the laser field. In spite of a compelling analysis, it still suffers from the disadvantage of inability to determine the initial wavepacket of electrons in its bound state, which is crucial in calculating Wigner delays. Argon and krypton are two complex systems that cannot be solved completely using 3D-TDSE. In experiments such as these, where precision is highly significant, it is necessary for one to closely examine the effects of approximations considered. Also, the effect of electron-electron correlations on the angular offsets were not discussed keeping the interpretation of the tunnelling times in jeopardy. In addition to that, Ar and Kr have very different ionization potentials, which could have resulted in different distributions of ionization times within the relatively long
3.3 Motivation for attoclock with H

The motivation for the project presented in this thesis stems from the idea that an experiment with atomic hydrogen could possibly resolve the debate, as it requires no assumptions on tunnelling models to simulate the attoclock experiment using 3D-TDSE and those precise simulations can be compared with the experimentally measured offsets. The hydrogen atom serves as a physical two-body system that can be treated analytically (in the non-relativistic approximation) and yields solutions in closed form. It has been long known that atomic physics experiments performed with H could be used as a point of reference for our understanding of the inherently complex dynamics of light-matter interactions.

The relevance of atomic hydrogen in benchmarking strong-field physics was demonstrated experimentally [38] and with an excellent agreement between theory and experiment. In addition to the calibration of absolute CEP presented in 1.5, few-cycle laser pulse intensities were calibrated within an accuracy of 1% [39]. By possessing knowledge of the right pulse parameters such as intensity and CEP, in the case of few-cycle laser pulses, it is possible to explain and interpret the experimental results unambiguously. Unfortunately, atomic H is not naturally available in the earth’s atmosphere and is a challenging task to produce in the lab. A secondary calibration standard was created using noble gases to this end [40], that can benefit labs elsewhere.

Therefore, H offers unparalleled opportunities for benchmarking such experimental and theoretical techniques in strong field physics. Careful experiments on H can yield data that quantitatively agrees with the theoretical predictions to within experimental uncertainty. Both the data and the predictions are validated by such agreement. With such advantage, we now utilise H in measuring and understanding tunnelling delays.

There were theoretical studies done to this end, but they too differed in their predictions [120–122]. While [120] and [122] proposed instantaneous tunnelling, [121] calculated various well-known tunnelling times including the one formulated using laser pulses used in those experiments.
Bohmian mechanics. All of these turned out to be non-zero according to their model. Zimmermann et al. [121] argue that Larmor time is the right choice of tunnelling model that one should use to describe scenario like AAS and predict $\sim 100$ as as tunnelling time in atomic H. However [122] used 3D-TDSE simulations to calculate the asymptotic MD of electrons from H and then later used classical back-propagation technique to infer the initial conditions for the electron at the tunnel exit. By doing so, they could not only determine tunnelling time to be instantaneous but also provided a relation of how the calculated angular offsets can be used to infer the proper tunnelling times. They concluded that most of the tunnelled fractions of electrons tunnel instantaneously. However, in the following thesis we use the methodology along similar lines as [120] to determine tunnelling delays using atomic hydrogen experimentally and to provide some invaluable insights towards resolving the debate regarding the angular offsets and its relation to the tunnelling times in strong field ionisation.

3.4 Summary

A brief introduction to strong field ionisation was presented with discussion of multiphoton ionisation and tunnel ionisation, whose regimes could potentially be separated using the Keldysh parameter. Later, the topic of interest– tunnel ionisation was discussed with regards to the relevant semi-classical model and its corresponding tunnelling times: Keldysh time $\tau_{kel}$ and symmetric time $\tau_{sym}$. Furthermore, the technique of AAS or attoclock was presented referring to its simplicity in its conception and utility in inferring tunnelling times. Further, a brief history of all the attoclock experiments were reviewed with the possible complications involved in interpreting their results. Finally the current status of the problem is discussed with emphasizing the necessity and motivation for performing attoclock experiment with atomic hydrogen.
4.1 Introduction

The following chapter deals with the experimental apparatus used for the technique of AAS. We begin the chapter with a description of a few-cycle laser system, that is central for the intense light-matter interaction. Although, the titanium doped sapphire (Ti:sapphire) femtosecond laser system is commercially available (FEMTOPOWER Compact pro CEPhase), it is not a turnkey system and each optical section has to be carefully aligned separately to obtain optimal experimental pulses. The third section of this chapter describes the construction and working of the atomic hydrogen source that uses a RF discharge to dissociate molecular hydrogen to its atomic form. Later in the section, a brief description of construction and working of the particle imaging system- REMI, is presented. The last section comprises of the pulse characterization and measurement mechanism and estimated peak intensity measurements.

4.2 Ti:sapphire laser system

The femtosecond laser (FEMTOPOWER CompactPro CEPhase) used is part of the Australian Attosecond Science Facility located at center of quantum dynamics, at Griffith University. This is a commercially available laser system that is capable of producing light pulses of pulse widths consisting of few oscillations of the electric field at around 780-800 nm wavelength.
Figure 4.1: Optical layout of FemtoPower Compact Pro. Figure is adopted from [123].
There are four major optical sections of the laser system as shown in Fig.4.1: (I): The oscillator and stretcher producing few cycle pulses in a Ti:sapphire crystal, which is later stretched to picosecond timescale by stretcher. This is then used as a seed pulse into the amplifier section. (II) A multi-pass amplifier, which performs amplification of stretched pulses through a second Ti:sapphire gain medium, (III) a prism compressor to compress the pulses back to 28 femtoseconds and finally (IV) a hollow core fiber along with broadband double chirped mirror or dispersion compensating mirror (DCM) set to spectrally broaden the amplified pulses to the few cycle regime.

4.2.1 Mode-locked oscillator and stretcher

The schematic arrangement of the oscillator optical cavity is shown in the Fig.4.2. The oscillator accommodates the optical resonator facilitating mode-locking with a spectral band width of \( \approx 240\text{nm} \) centered around central wavelength 790 nm and short temporal duration at high repetition rate of 80MHz. It is a Kerr-Lens mode-locked system with mirror dispersion control (Femtolasers Rainbow) [4]. The oscillator uses a doped Ti:sapphire crystal whose temperature is maintained at 292K by a controlled water cooling system. It is pumped by a 532 nm laser (Coherent Verdi V-5) with power \( \sim 3 \) W. The pump laser goes through a glsao (model:AFM-405A1), used to modulate the intensity of the pump power for locking the carrier-envelope offset frequency discussed in section(2.2.2).

Two asymmetric arms: long and short with two focussing mirrors form the laser cavity. The end of the cavity are an end cavity mirror and an output coupler that is partially transmissive mirror placed at 10° to avoid back reflection. Any extra group delay dispersion (GDD) introduced in the cavity is compensated by a a comparable wedge placed just behind the output coupler. A pair of DCMs introduce an extra negative GDD which is later compensated with a pair of fused silica wedges on a translation stage. This allows for a fine control over the cavity dispersion as close to zero as possible. There are couple of adjustable screws that allow the oscillator to operate in two configurations. The first screw is attached to the platform on which the gain medium is mounted, used for a good overlap between the pump and cavity mode. The second one attaches to the one of the cavity focussing mirrors and
Figure 4.2: An illustration of the oscillator in the current laser system. Verdi V5 laser is used to pump the gain medium. Oscillator consists of two arms, one long and one short, containing internal wedges for adjusting the dispersion. The modelocked pulse is extracted from the output coupler. This is then directed into stretcher after passing through periodically poled magnesium oxide doped Lithium Niobate (PPLN) crystal. A small part of light is used to produce CEP offset frequency signal that is fed into the CEP locking electronics for giving a feedback to acousto-optic modulator (AOM). Figure is adopted from [124].

defines the stability range of the cavity mode. With both the screws in their extreme position (wound out), we align the cavity to get maximum CW power (∼ 450 – 500 mW). Once maximum CW is achieved, the first screw is optimally wound in to around 420 mW, to ensure Kerr lensing. The stability range (focussing mirror) is then wound in with simultaneously rocking back and forth the cavity end mirror to introduce perturbation leading to a Kerr-lensed modelock configuration. A stable mode used for the current thesis is around 200-220 mW of power, 80 MHz repetition rate and with a broad spectrum around 780-790 nm corresponding to sub 7 fs pulse. If this simple procedure is not enough to get a stable mode lock, then the position of the gain medium is readjusted and the above process is repeated till we attain a stable mode.

The laser beam is than focused onto a periodically poled magnesium oxide doped
Figure 4.3: A schematic of the pulse stretcher in the laser system. As part of CPA, the few-cycle pulse generated in the oscillator is stretched temporally before injecting into amplifier. TOD mirrors are used to pre-compensate the third order dispersion which will be acquired in the amplifier section. A photodiode is used to measure the oscillator repetition rate and a part of it goes to the CEP locking electronics. Adopted from [124].

Lithium Niobate PPLN frequency doubling crystal, generating $2f$ light. A small fraction of the light goes to the $f - 2f$ interferometer, giving a carrier-envelope offset signal detected on an Indium-Gallium-Arsenide InGaAs (MenloSystem FPD510) avalanche photodetector (APD). The locking electronics (Menlo XPS800) is used to process the offset signal, which provides a feedback signal to AOM, modulating the pump beam. The rest of it goes to the stretcher section to prepare for amplifier seed. A mirror is used before the stretcher section directing a part of the light to the fibre spectrometer (Ocean Optics USB4006) to ensure the correct spectrum for operation and also to the power meter for measuring optical power.

As part of CPA, the few-cycle femtosecond pulses are stretched to picoseconds using the stretcher section. The stretcher section is shown in Fig.4.3. Femtosecond pulses pass through two pairs of factory tuned third-order dispersion (TOD) compensating mirrors before getting temporally chirped to 90 picoseconds by a 5 cm Schott SF57 glass. By temporally broadening the pulses, the pulse energy drops keeping the gain medium in the multi-pass amplifier safe. The light is retro-reflected back onto the TOD compensating mirrors to pre-compensate TOD gained in the amplifier section. These are the seed pulses injected into the amplifier section. A
CHAPTER 4. EXPERIMENTAL APPARATUS

Figure 4.4: The stretched modelocked pulse from the oscillator is fed as the input into the multi-pass amplifier section. The beam gets amplified through the Ti:sapphire crystal, used as the gain medium, by passing through 9 times. A Pockels cell is used to extract the amplified pulse such that the repetition rate is 1 KHz. Figure taken from [123].

second photodiode is used to sample a fraction of the seed beam for measuring oscillator’s repetition rate and synchronising with amplifier and CEP lock electronics.

4.2.2 Multi-pass amplifier

Multi-pass amplifier is the second section of the few cycle laser system. The schematic is shown in Fig.4.4. It works on CPA as described in Sec.1.1.2 to amplify the seed beam from oscillator. A Ti:sapphire crystal is used as the gain medium which is enclosed in a vacuum chamber having Brewster windows on either side for light to enter and exit. It is cooled to 238 K using a Peltier for optimal gain. Water lines run around the base of the vacuum chamber with water at 19°C acting as a coolant to drain the heat. A Nd:YLF Q-switched laser system (model: Coherent Evolution-15) pumps the amplifier gain medium with 6-7 W at a repetition rate of 1 KHz. The seed beam is amplified serially by passing through the crystal for 9 times. An entire 80 MHz train from oscillator is amplified in the first four passes followed by a pass through Pockels cells. A single pulse is isolated and amplified in the remaining five passes by using a polarizing beam splitter (PBS) and high voltage Pockels cells which also reduces the repetition rate of the laser to 1 KHz. Pockels cells is placed in such a position that it would also help to reduce the amplified spontaneous emission.
contribution. Berek compensator is used to gain a contrast ratio of 10000:1 amplified pulse to the background. The final output from the amplifier is $\sim 1.1 \text{ W}$ of power with 1 KHz repetition rate (energy of 1.1 mJ).

### 4.2.3 Prism compressor

The prism compressor as shown in Fig. 4.5 is used to compress back the amplified temporally chirped pulses to 28 fs. It primarily comprises of two Brewster angled glass prism pairs [125] separated by $\sim 5$ m of air path. These prisms introduce low GDD and TOD into beam path. One prism pair is mounted on an angular translation mount that allows for the amount of GDD given to the pulse to be altered. The spatial dispersion is properly reversed by letting the beam be retro reflected back through the prism. The typical output from the prism compressor is 850 µJ.

### 4.2.4 Hollow-core fiber with DCM’s set

A hollow core fiber filled with neon gas in combination with DCMs are used to further compress the <30 fs pulse from the prism compressor to few-cycle regime [126–128]. The hollow core fiber is essentially a 1 metre long fused silica capillary tube placed on a V-grove, inside a vacuum tube evacuated using a Pfieffer MVP015-2 diaphragm pump. The pump is connected via a valve and is kept closed under operation. Soon after evacuating, the tube is filled with neon gas and kept at a constant pressure of $\sim 2 - 2.5$ bar. Neon serves as the non-linear medium wherein the process of SPM broadens the spectrum [129,130] and high ionization energy of neon helps to minimize the multi-photon process inside the capillary which is sub-optimal for SPM.
CHAPTER 4. EXPERIMENTAL APPARATUS

Figure 4.6: Schematic diagram of a hollow core fiber with DCM set used to compress the 28 fs pulses to few-cycle regime. A set of fast steering mirrors together with Thorlabs apt-quad photo detectors are used to stabilise the beam coupling into the fiber. Adopted from [124].

procedure. Evacuating vacuum tube beforehand helps in reducing impurities which can affect the spectral broadening process.

The light pulses from the prism compressor is coupled into the fiber using a lens of focal length $f = 1000$ mm through a thin view port placed at Brewster angle. The primary source of the instability caused to the fundamental mode propagating in the fiber is due to the beam pointing fluctuation. Also the focused beam pointing erroneously can damage the fiber input easily. A beam stabilization system comprising of two sets of Thorlabs apt-quad photo detectors and Newport FSM–300 series fast steering mirrors are used to maintain the input beam at a steady position. These are placed at the exit of the beam from prism compressor and before the entrance of the beam into the fiber as shown in the Fig.4.6. For the alignment of the focused beam inside the fiber, a pair of x-y translators are attached to the
vacuum tube.

The fibre output passes through another thin Brewster window before it is collimated through a concave spherical mirror of focal length $f = 750$ mm. Although SPM broadens the spectrum, it is not Fourier limited pulse. The pulse train is then compressed by eleven reflections on double chirped mirror. The multi-layered DCMs are used to compensate any positive GDD gained through the fiber compressor unit and reduces the pulse duration to 6 fs. They are also used to create an excessive negative GDD that can be controllably compensated using a pair of fused silica wedges later at the experimental end-station. The final output from the fiber and DCMs is $300\mu$J of energy, $<6$ fs pulse duration at a repetition rate of 1 KHz is obtained.

4.3 CEP stabilization

The constructive interference of a large number of coherent longitudinal modes in the oscillator gives rise to ultra-short few-cycle pulses. The phase difference between the carrier wave travelling with phase velocity and the envelope propagating with group velocity is referred as the CEP offset, $\Delta \phi$. The mismatch between the phase and group velocity due to as the pulse propagates through non-linear optical components

Figure 4.7: An illustration of CEP offsets that vary from pulse to pulse due to a mismatch of phase and group velocity. The figure is taken adapted from [131].
and thereby dispersion caused by it shifts the $\Delta \phi$ rapidly as shown in Fig.4.7. Finally, a constant phase shift is acquired from pulse to pulse due to the refractive index of the gain medium. The CEP offsets are measured and controlled using frequency combs [25,132,133].

### 4.3.1 f-2f interferometer for CEP locking

A series of equally spaced, discrete frequency lines is known as an optical frequency comb. The Fourier transform of a pulse train would yield a frequency comb of longitudinal modes, with separation equal to the repetition rate $f_{\text{rep}}$. This is illustrated in Fig.4.8. The $n^{th}$ discrete frequency line in the comb are related to the CEP offset $\Delta \phi$ [25] as following:

\begin{align}
    f_n &= nf_{\text{rep}} + f_0, \quad \text{with} \\
    f_0 &= \frac{1}{2\pi} \Delta \phi f_{\text{rep}},
\end{align}

where $f_n$ being the $n^{th}$ line in the comb and $f_0$ being the mode for $n = 0$. It is trivial to see that the displacement of $f_0$ from 0 would give the information of the CEP offset.
Figure 4.9: A schematic of \( f - 2f \) interferometer used for ‘slow phase lock’ as part of CEP stabilisation set-up in the experiment. figure adopted from [124].

In order to infer carrier-envelope offset frequency \( f_0 \), we use the \( f - 2f \) interference technique as developed by Nobel laureates H"{a}nsch and Hall and is called \( f - 2f \) interferometer [134, 135]. As part of this, the frequency comb is passed through a frequency doubling crystal generating the second harmonic frequency comb, with the modes related as

\[
f_{n(\text{SHG})} = 2(nf_{\text{rep}} + f_0).
\]  

(4.3)

Given the broad spectrum of the fundamental frequency mode, that can span all the way from \( f - 2f \) exceeding an octave, it is possible for the blue end of the fundamental frequency comb lines to interfere with the red end of the second harmonic comb lines as illustrated in Fig.4.8. This yields a beat signal giving us the offset frequency

\[
f_{n(\text{SHG})} - f_{2n} = (2nf_{\text{rep}} + 2f_0) - (2nf_{\text{rep}} + f_0) = f_0.
\]  

(4.4)

4.3.2 Stabilization of CEP

The phase stabilisation method used in our laser system is based on monolithic locking technique [136], which is different from the above \( f - 2f \) interferometer. The locking scheme is called the fast phase lock, since it operates at RF frequencies > 10 KHz. The pulse train is passed through a PPLN crystal, generating \( \geq 1350 \text{ nm} \) spectral components due to difference frequency generation (DFG) and SPM. A beat signal is generated when the DFG signal is interfered with the fundamental frequency comb components on an indium gallium arsenide (InGaAs) APD. The beat signal is fed into the locking electronics (Menlo: XPS800) that produces an error signal to AOM. The error signal from AOM modulates the intensity of the pump beam, affecting the
non-linear Kerr effects and eventually the refractive index of the Ti:sapphire crystal. This is used to correct the phase slippage caused due to the mismatch in group and phase velocity of the pulse. Because the stabilization range of the locking electronics is small, the intra-cavity wedges are used for coarse adjustment of the CEP. The carrier-envelope offset frequency is locked to one quarter of the repetition rate of the oscillator, such that every fourth oscillator pulse has identical CEP.

The later part of the CEP stabilisation is done near the experimental end-station, at a frequency identical to the repetition rate of the laser. Thermal fluctuation of the amplifier crystal can lead to slow drifts in CEP and hence this second slow lock is necessary such that every single pulse has an identical CEP. This is done by using a $f - 2f$ interferometer (Menlo:APS800). A schematic of this set up is given in Fig. 4.9. A super continuum white light is created by focusing the laser light into the sapphire plate, followed by SHG process. These signals are interfered that is measured using a USB spectrometer. The computer software generates a voltage offset from the analysed interferogram which is fed back to the fast phase electronics. In addition to the adjustment of internal cavity wedges, the software can help lock and scan electronically a range of $4\pi$ phase.
4.4 Pulse characterization

The few-cycle pulse is characterised using an interferometric autocorrelator (Femtometer F1A) or also known as fringe-resolved autocorrelation (FRAC) introduced by Jean-Claude Diels [137]. This technique extracts the pulse duration by measuring both spectrum and autocorrelation signal. The measurement comprises of acquiring the second harmonic intensity from a coherent superposition of the fundamental split beam as a function of variable temporal delay. In other words, the measurement is a self referencing technique that relies on the extent of overlap of the pulse by its identical copy.

The optical layout is shown in Fig.4.10. The scheme involves a Michelson interferometer with one of the arms seated on a electrically driven piezo stage. The the piezo stage is controlled by the electronic box and software provided by Femtolasers. A 50:50 beamsplitter of 1 mm thickness with partially coated on either side is used to split and mix the light from both the arms. A variable time delay $\tau$ is introduced between the two pulses by driving the piezo stage which introduces temporal interference of the two beams. The interfered signal is then focussed onto a SHG crystal using a parabolic silver (low GDD) mirror. The SHG signal is passed through a low pass filter, filtering the fundamental, which eventually is collected on
a photodiode. The pulse duration is defined as FWHM of the intensity envelope of the laser pulse.

4.5 Atomic hydrogen source

One of the necessary components of the experiment are the target species: atomic and molecular hydrogen. Molecular hydrogen is fairly straightforward to acquire commercially in the form of pressurised gas bottles with 99.999% purity. The gas from the gas bottle is then delivered into the interaction chamber by turning it into a supersonic cold gas jet using vacuum system and skimmers. However, producing a stable and robust atomic hydrogen gas jet is non-trivial. Although, atomic hydrogen is found in abundance in the interstellar space, it is quite rare in the earth’s atmosphere. Atomic hydrogen is chemically highly unstable and thus spontaneously interacts with other H atom to form a hydrogen molecule. This is said to be one of the strongest chemical reactions in the universe and thus poses a great challenge in creating a stable H source.

The first discharge tube to produce an atomic H beam was created by Wood in 1920 [138]. Later, several methods were previously employed in producing the atomic H beam by using microwave discharges [139,140], arc discharges [141], thermal cracking [142] etc. Although these sources were capable of producing H beam with $\sim 80\%$ efficiency, they had their shortcomings in form of the large input powers, being too bulky and higher temperatures of H ($> 10^3 - 10^4 K$). These disadvantages were overcome eventually by RF discharge sources [143]. They were shown to produce H with an efficiency of $> 95\%$ with lower temperatures of H (500 K) using low Rf drive power (few tens of watts). The current thesis employs one such RF-discharge H source that was initially developed and graciously donated by Prof. Daniel Kleppner’s MIT lab.

4.5.1 Construction of H source

The RF discharge source architecture is on the similar lines as [143]. A water-cooled Pyrex glass discharge tube is inserted into a shielded quarter wave helical resonator as shown in Fig. 4.12. Molecular hydrogen flows through the central bore breaking
down into its atomic form in the bulbous region shown in pink colour in the figure. The driving pressure of H$_2$ is controlled by a leak valve (Granville Phillips 203). The inner diameter of the central bore is 5 mm with its length being 20.5 cm. The bulbous region is about 85 mm from the input end and of length 70 mm. The pink colour of the discharge seen is due to the Balmer transitions in H. The central region is cooled with chilled water using a closed loop system (ThermoTek T255P) that also provides a handle on the circulating water’s temperature in the range of 10$^\circ$-20$^\circ$. In addition to cooling the heated discharge tube, it also aids in reducing the rate of surface recombination of of atomic hydrogen to its molecular form, as Pyrex glass known to have recombination coefficient that decreases rapidly with the decreasing surface temperature in the range of 120 K-500 K [145].

The helical resonator, designed as per the specifications of MacAlpine [146], is used to couple RF power to the gas medium. The resonator is formed by a copper coil placed inside a cylindrical conductive shield as shown in Fig.4.13. One end of the coil is short-circuited to the shield (point X) whilst the opposite end (point Y) is
Figure 4.13: A schematic of the quarter-wave helical resonator, featuring a copper coil surrounded by a cylindrical conductive shield. The coil is short-circuited to the shield at point X, open-circuited at point Y, and the RF input is applied at point Z. Table (2.1) contains the values for the important dimensions that are labelled on the resonator. Adopted from [144].

left unattached, forming an open circuit. An RF voltage is applied to the coil using a BNC soldered at point Z and the shield is grounded. When resonance is achieved, the length of coil between X and Z is seen as having a high impedance, causing a standing wave to form between the two points Y and Z of the coil.

The dimensions of the resonator are: \( a = 13.2 \text{ mm} \), \( b = 38.8 \text{ mm} \), \( c = 15 \text{ mm} \), \( d_0 = 2.2 \text{ mm} \), \( d_1 = 50.8 \text{ mm} \), \( d_2 = 28.6 \text{ mm} \), \( e = 4.1 \text{ mm} \) and \( f = 67 \text{ mm} \). The quality factor \( Q \) can be calculated using the relation

\[
Q = 1.97d_1\sqrt{f_0},
\]

with \( d_1 \) in mm and \( f_0 \) being the resonance frequency in MHz. The theoretical and measured unloaded \( Q \) values were \( \sim 1000 \) and \( \sim 350 \) respectively with \( f_0 \approx 99 \) MHz [144]. While the discharge is operating, the \( Q \) value drops to \( \sim 20 \) with \( f_0 \approx 75 \) MHz.

With the help of a voltage-controlled oscillator (VCO) (Mini-Circuits ZOS-100+), 75 MHz seed RF signal was generated. A simple voltage divider circuit with a 9 V battery was used to tune the frequency in the range of \( \sim 4 \) MHz around the 75 MHz central VCO frequency. The seed signal was amplified to 17 W by an RF amplifier (Amplifier Research). To optimize the coupling of the amplified RF seed to the resonator, a coaxial bi-directional coupler (Mini-Circuits ZFBDC20-62HP-S+) was
Figure 4.14: Schematic for measuring the intensities of the atomic H and molecular H$_2$ spectral emission lines. Light from the discharge source travels through a small viewport and is coupled into a multi-mode fiber via an aspheric lens. This fiber is coupled to a CCD spectrometer after which the signal is fed into a PC. Adapted from [41].

used to measure the reflected RF power. An on-resonant VCO frequency produced the brightest pink discharge, with less than 1.5% reflected power. In contrast, an off-resonant VCO frequency produced a visibly dimmer discharge, with up to 28% reflected RF power at the extremes of the VCO tuning range.

The left-hand side (in Fig.4.12) of the resonator shield is welded to a 6” Conflat (CF) flange with a through-hole for the discharge tube to slot through. The flange is attached to the vacuum system which houses the discharge source. A teflon spacer is used to locate the discharge tube inside the resonator and also prevent damage to the otherwise fragile tube. The vacuum seal to the tube is maintained by an o-ring and clamp on the right-hand side of the shield. Therefore, the inside volume of the shield is kept at atmospheric pressure.

### 4.5.2 Dissociation fraction

The partial molar fraction of H present in the mixture of H$_2$ dissociated and undisassociated molecules is defined as the dissociation ratio,

$$\mu = \frac{[H]}{[H] + 2[H_2]},$$

(4.6)

Here $[H]$ is the number density of hydrogen atoms in its $1^2S_{1/2}$ ground state and $[H_2]$ is the number density of the hydrogen molecules in the $X^1\Sigma_g^+$ ground state, which encompasses all the rotational-vibrational energy levels. In order to determine the efficiency of our source, we measure the dissociation fraction using emission spectroscopy as proposed [147] and verified experimentally in [148] by Lavrov et al.

The method relies on the assumptions that (I) excitation of H and H$_2$ is pre-
dominantly by electron impact, which eventually get to their ground states by spontaneously emitting photons and (II) the electron energy distribution function is approximated by a Maxwellian function that has an effective electron temperature \((T_{e}^{eff})\). This would imply that the number densities \([H]\) and \([H_2]\) are directly proportional to the intensities of the spectral lines emitted due to the de-excitation processes. In practice, measuring 5 spectral lines is sufficient to estimate \(\mu\). The 5 lines are the Balmer series of H i.e. \(H_{\alpha}\) (656.3 nm: \(n = 3 \rightarrow 2\)) and \(H_{\beta}\) (486.1 nm: \(n = 4 \rightarrow 2\)); and the \(Q_1\) (622.48), \(Q_2\) (623.03) and \(Q_3\) (623.84) lines of the (2-2) \(Q\) rotational series of the \(H_2\) Fulcher-\(\alpha\) series from the \(d^3\Pi_u^-, v = 2, N\) excited states to the \(a^3\Sigma_g^+, v = 2, N\) ground states. The Fulcher-\(\alpha\) lines provide us with the information of the gas temperature inside the discharge tube which is later used with the relative intensities of \(H_{\alpha}\) to \(H_{\alpha}\) and \(Q_1\) giving us the dissociation fraction \(\mu\).

A CCD spectrometer (Ocean optics HR4000) is used to measure the intensities of the above mentioned spectral lines, connected through a USB to the PC as shown in the schematic in Fig. 4.14. The spectrometer responds from 478-684 nm with a 0.2 nm resolution. Since the \(H_2\) lines are weaker than the Balmer series lines, variable integration time is used to measure the intensities. This is taken into account appropriately later while we calculate the relative intensities, gas temperature and eventually \(\mu\). The dissociation ratio was measured to be \(\sim 50\%\) while performing the experiments pertaining to the current thesis. The current source in the lab is quite an established and robust set-up and hence a detailed explanation in regards to the theory and measurement behind determining dissociation ratio, optimizing the discharge source and set-up can be found in [41,144].

### 4.6 Reaction microscope

The momenta and energy of the ionized fragments bear the signature of strong-field interaction. These kinematic quantities are measured using a REMI. Unlike the TOF mass spectrometer described in Chapter 1 that can measure only scalar kinematic quantities confined to ions or electrons in a certain solid angle, REMI can help us in reconstructing the 3D momentum vectors of the ionised fragments by detecting in almost \(4\pi\) solid angle. As the name suggests, REMI got widely popular for its
ability to measure various ionised fragments of complex molecules and electrons simultaneously, revealing the dynamics of chemical reactions [149]. It is capable of measuring momentum with a superior resolution of a fraction of atomic unit and hence was termed as the ‘the bubble chambers of atomic physics’. More details can be found in [149–154]. The supersonic gas jet beam line, position sensitive, multi-hit detectors, uniform electric and magnetic fields are the main components that form the REMI. The following section briefly outlines the basic working principle of REMIs starting with description of the typical set-up as used in this work and data processing procedures.

4.6.1 REMI setup

The REMI is traditionally known as COLTRIMS abbreviated for Cold Target Recoil Ion Momentum Spectrometer. A schematic of REMI is shown in Fig.4.15. The REMI used in the Australian Attosecond Science Facility at Griffith university is a commercially available device from RoentDek. Here, we would like to explain the set up that existed during its installation.

The REMI has a source chamber for the gas inlet and two differential chambers followed by the main chamber which is the interaction region. The gas jet becomes supersonic and is internally cold (having almost no transverse velocities) as it travels through a system of nozzle, skimmer and attenuating slits. An ultra-high vacuum of \(1 \times 10^{-9}\) Torr is achieved using the turbo molecular pumps Pfieffer TMU521YP, backed up by a Pfeiffer HiCube 80 Eco pump package that consists of a HiFace 80 turbomolecular pump and a backing pump. In addition to this, the chamber is baked to a temperature of 120 – 130°C, so as to remove any presence of adsorbed water vapour in the system that is eventually pumped out through the turbomolecular pump and the non-evaporable getter pump (Gamma Vacuum NEG300) is installed onto the main chamber. Getter pumps primarily are cartridges that have a reactive surfaces on it that help either trapping gases by a chemical reaction or by adsorption. It is recommended to maintain a pressure of \(<1 \times 10^{-8}\) Torr for maintaining longevity of the cartridges and in the current thesis, it is used primarily to reduce the background hydrogen gas. The pressure in the main chamber eventually goes down to \(<5 \times 10^{-10}\) Torr (as calibrated to \(N_2\) gas), where the experiment is performed.
CHAPTER 4. EXPERIMENTAL APPARATUS

Figure 4.15: A schematic layout of REMI is shown, where the intense laser-matter interaction is studied. The supersonic skimmed gas jet (shown in green) interacts with the focussed laser beam under uniform electric (by spectrometer) and magnetic fields (provided by Helmoltz coils). The ionised charged fragments (ions in red and electrons in blue) reach their respective detectors giving us the information of their momenta and energy. Figure is adapted from [155].

The REMI’s main chamber is equipped with another gas line integrating the atomic hydrogen source. This is attached opposite to the above discussed commercially installed supersonic gas line, described in detail in Chapter 5.

To facilitate the intense light-matter interaction in the interaction region a spherical mirror of focal length $f = 75$ mm is placed inside the main chamber, with a vacuum compatible 3-D translation stage attached to it. The mirror is mounted onto a base plate that is connected via a bellow, with an external manual control using micrometers. This allows to adjust the mirror alignment in situ such that the light focuses onto the atomic/molecular beam.

After the supersonic gas jet and the focussed light beam allows for the strong-field ionisation, the next important aspect of REMI is to extract these ionised fragments. REMI utilises a mass spectrometer for creating a uniform electric field and Helmoltz coils for uniform magnetic field in order to accelerate the positive and negatively charged ionised fragments towards their respective detectors.
Figure 4.16: An illustration of the REMI spectrometer where a series of narrowly equidistant copper plates with holes are used. These copper plates are connected with resistors such that a constant potential difference is maintained between the successive plates. Ion and electron time-position sensitive detectors (consisting of MCP and DLDs) are placed at top and bottom of the spectrometer, respectively. The spectrometer is oriented perpendicular to both gas jet and laser beam. The laser is focused using a spherical mirror of focal length $f = 75$ mm. Figure is taken from [124].

A schematic of the spectrometer is shown in Fig.4.16. The spectrometer comprises a series of copper plates with holes in the middle separated by a narrow gap, connected by resistors. The two ends of the spectrometer (which is $\sim 25$ cm apart) is kept at an appropriate potential difference using a dual high voltage supply module (2×4 KV iseg NHQ 214M), with constantly increasing potential difference between the successive copper plates. The voltage is varied depending on the temporal (or momentum) resolution that an experiment demands. The geometry of the copper plates and the distance between the plates is chosen in such a way that a uniform electric field is generated in the spectrometer. The interaction region is approximately around 1/3rd its way from one of the ends, where negative potential is applied. The positively charged ions accelerate along this direction, with electrons accelerating...
through 2/3rd of the spectrometer towards the opposite end. There are time and position sensitive detectors (TPSD) placed on either end of the spectrometer, that extract the ions and electrons. Therefore, the direction of spectrometer defines the TOF direction and it is placed perpendicular to both laser beam direction and supersonic gas jet. The electrons’ collection efficiency is improved in 4\pi solid angle by applying a uniform magnetic field along the TOF direction using circular Helmoltz coils as shown in Fig.4.15.

The TPSD comprises of MCPs of radius 80 mm in combination with RoentDek delay line detectors (RoentDekDLD80). The detection is performed in two steps: the first step involves the ion/electron hitting the MCP that is biased using iseg NHQ214M. MCP then creates an electron cloud, giving the information of the arrival time of the particle. The second step involves the delay line detector measuring the centre of gravity of this electron bunch with a spatial resolution of < 0.1 mm.

A delay line detector works on the principle that when a particle or electron bunch hits the transmission line the delay in the signals arrived at either end of it is dependent on the position of the hit [156]. A schematic of a 2-axis delay line detector is shown in 4.17. It is typically made by wrapping up a helical or spiral wire to a base plate made of aluminium or ceramics. One wire being the “signal” wire receives the electron bunch and other is “reference” wire that is capacitatively coupled to pick up the signal. Typically, the signal wire is maintained at a higher potential than the reference wire. The signals then used by a pair of differential amplifiers contained with in a RoentDek ATR19 constant-fraction-discriminator module that generates a signal based on arrival time difference \( \delta t \). This signal is then used with the correct calibration of the timing unit to map the 2D position of the particle hit on the delay line. The detection of multi-hits is generally limited by the electronic pulse duration i.e. if the time-of-arrival of two hits is within the electronic pulse duration, the information of both the particles is ambiguous. To increase this multi-hit capability, an extra layer is wrapped above the two layers that can unambiguously detect multi-hits unless both the particles hit at the same position and instant [157].

The electron detector works using such a delay-line detector, RoentDek HEX75 where three delay line detectors are used with a relative angle of 60\(^\circ\) each.

The multi-hit signals from the TPSD are digitised using the 8 channel time-to-
Figure 4.17: The electron cloud (red dot) produced in MCP is incident on the two wire grids that are on each other but not connected. One of the wires being signal and the other being reference. The signal reaches on either end with a delay measured by the DAQs shown. The measured $\delta t$ time difference is used to infer the position where electron impact. Figure adopted from [124].

digital converter with a temporal resolution of 25 ps/bin, controlled by PC-RoentDek TDC8HP. This has the information of the distance between the wire pair at which the electron impact occurs, which can be used to infer the x-y coordinates of the charged particle by manufacturer’s calibration. The TOF signals are acquired using the acquisition and control boxes that consist of FAMP8, constant fraction discriminator CFD8c and the ATR-19. The trigger is provided from the fast photodiode signal present in the amplifier section in the laser. Hence, events are recorded for every single pulse coming from the laser. In addition to the RoentDek TDC8HP hardware, Cobold PC software is provided using which the momentum of the ionised fragments can be reconstructed using the position and time of arrival keinformation of the fragments with the set electric and magnetic field parameters used in the experiment.

4.6.2 Data processing

RoentDek provides the software package Cobold PC that can be used to reconstruct the 3D momenta of the detected fragments from the raw data. The software also
allows the users to script codes on Visual Studio platform that helps in both post processing data and real time visualisation for coincident measurements. Later, the processed data is presented in form of various histograms and line plots like $m/q$ ratio, 2D positioning and 3D momentum of detected ions and electrons, that are of the user’s interest. In addition to this, the graphically represented data are export-friendly in ASCII format which can be further analysed in MATLAB or Mathematica.

4.7 Estimated peak intensity

Estimating the peak intensity of the light pulses is a crucial parameter in understanding strong-field phenomena. The straightforward way of calculating peak intensity is from the average power, pulse duration, repetition rate and the spot size of the focused beam. The error in determining intensity using this method can be huge since focal spot size and the effect of chirp on pulse duration and peak intensity cannot be accurately determined. Hence, it is advised to measure the ionisation cross-sections or photoelectron momentum spectra that carry the signature of the light pulses with them. The current thesis, adopts the in situ technique of determining peak intensities using recoil momentum of ions/ streaking momentum of photoelectrons under strong field ionisation with circularly polarised pulses. Details and theory of the method can be found in [158]. Atomic hydrogen is used as the target species and the ions/electrons are detected in coincidences in REMI. The magnitude of the drift momentum gained is directly proportional to the peak electric field.

$$P_o = \sqrt{P_x^2 + P_y^2} = \frac{eE_0}{\omega}$$

(4.7)

where $E_0$ and $\omega$ are the peak electric field amplitude and angular frequency of the circularly polarized light, respectively. While the error in the former method of estimating peak intensity (by measuring focal spot size, pulse duration and power) could be as high as 100%, the in situ technique typically suffers from 10% error.
The question of tunnelling times in general is still not well defined as was illustrated in Chapter 2. The reason is due to the underlying uncertainty in modelling time within the theoretical framework of quantum mechanics and the inaccessibility of the classically forbidden region directly for the experimentalists. However indirect techniques to measure the interaction time with the barrier could be utilised to validate various theories of tunnelling. This is also true in the strong field scenario, wherein the electron tunnels through the suppressed atomic potential to enter into the continuum. This process of tunnel ionisation was assumed to be an instantaneous process due to the very short traversal times of the electron across the barrier. The originally far-fetched goal of experimental access to tunnelling time now seems to be within reach because of the high precision measurements in real time made possible by ultrafast physics. AAS or attoclock, discussed in Chapter 3, is one such technique that is used to probe the information of the electron’s tunnelling time within an accuracy of a few tens of attoseconds, under strong field tunnel ionisation.

The ongoing debate in relation to the recent attoclock experiments and the difficulties in interpreting the measurements were reviewed in Chapter 3. One underlying reason behind the difficulties is that the experiments are performed in the $\gamma \sim 1$ regime. As discussed in Sec.3.1, in case of $\gamma \ll 1$, the potential changes adiabatically with the external strong-field and the quasi-static ionisation rates are used to explain the strong-field ionisation. However multiphoton ionisation and tunnelling regimes are not expected to have a sharp transition and generally both are assumed to be present in the intermediate regime with $\gamma \sim 1$. This would not allow for one to consider the potential to change in an adiabatic fashion and thus this regime is referred to as the non-adiabatic tunnelling regime [159]. While it has been possible to develop ionisation rate equations for each of the regimes (multi-photon and adiabatic tunnelling) separately, the non-adiabatic tunnelling regime remains
both theoretically challenging and experimentally interesting.

In the current chapter, we present the results of the attoclock experiment performed using atomic hydrogen that can possibly shed some light onto the tunnelling dynamics. The first section Sec. 5.1 provides a brief overview of the attoclock technique and the how the experiment with atomic hydrogen (H) can help us overcome the difficulties that other attoclock experiments suffer from. Sec.5.2 provides information about the the experimental set up and following section Sec.5.3 explains the nuances of experimental procedure and analysis that was done on the acquired data. Thereafter the results from the experiment are discussed with a brief overview of the theoretical simulations that went in to reach the conclusions from the experiment. Finally we conclude the chapter in Sec.5.5.

5.1 Introduction

‘Attoclock’ is a streaking technique that employs a near circular-polarised few-cycle infrared pulse acting as a clock in measuring the tunnelling dynamics. The evolving $\vec{E}(t)$ field vector, rotating by 360°, acts as a rotating minute’s hand that maps time to angle in the polarization plane. That single pulse provides both the ionizing radiation and the streaking field, therefore making the technique self-referencing. It was envisaged based on a two-step process, where the first step is tunnelling and the second step assumes a classical description of the electron-in-an electromagnetic-field (streaking) from the instant it appears in the continuum whilst neglecting the Coulomb potential of the parent ion. The very significant non-linearity of tunnelling ionization ensures that the ionization rate peaks when the $\vec{E}(t)$ field reaches its maximum $E_{\text{peak}}$. The streaking field drives the ionized electron in such a way that its final momentum (following the interaction with the pulse) is equal to the negative instantaneous value of the vector potential, $\vec{A}(t)$ of the streaking field at the moment of ionization. Hence, the technique involves a well-defined time-zero, which in this case is the direction of the maximum field, and also naturally encodes the information on the instant of ionization, the tunnel exit; thus providing the information on any possible tunnelling delays.

Previous experiments investigating tunnelling were performed on different targets
Figure 5.1: The temporal evolution of the field vector of a few-cycle pulse provides a unique direction of the maximal field vector in the polarization plane. A strong E-field can bend the atom’s binding potential, allowing for the electron to tunnel out. For a circularly polarized field the vector-potential trails the rotating electric field vector by $\pi/2$. Consequently, upon ionization, the electron will be emitted perpendicularly to the instantaneous direction of the electric field at the moment of ionization. However, any delay between the electron’s exit and an independently measured maximum of the E field manifests itself as an angular offset in the photoelectron momentum distribution (PMD). As the Coulomb potential introduces an angular shift to the electron momentum in a direction dictated by the right- or left-hand circularly-polarized streaking field, any additional delay due to the time spent by the electron under the potential barrier will result in a greater angular shift in the electron’s momentum and thus could be measured experimentally. As the field vector sweeps $360^\circ$ in 2.6 fs i.e., a single optical cycle for a 770 nm pulse, $1^\circ \approx 7.13$ asec in the electron ionization delay. Hence, by measuring the 3D PMD one can reconstruct the distribution of ionization time delays with respect to the time when the electric field reaches its maximum.
like Ar, Kr, and He. These target species are quite complex and interpretation of
the results relies on the theoretical approximations that one chooses in their models.
This makes it difficult to interpret the experimental results unambiguously. The
difficulties are primarily due to (i) the inability to perform \textit{ab initio} simulations with
exact potentials that can account for electron-electron correlations and (ii) relying
on semi-classical models that fail to estimate the contributions from long-range
parent ion-electron interactions. It is possible for one to avoid these complications
by choosing H as a target atom, since solving the 3D-TDSE for this atom requires
no assumptions beyond the dipole approximation in the non-relativistic regime.

The issue of multi-electron configuration in modelling the potential could easily be
overcome by using H. Though 3D-TDSE simulations can predict the exact values of
angular offsets, they lack the access to internal dynamics that we are interested in, i.e.
the long range interactions. Those simulations can not disentangle the contribution
of the Coulomb force on the electron due to the ion from the real tunnelling time to
the observed angular offsets. This was indeed the motivation for people to rely on
semi-classical models wherein the whole process can be analysed in two to three steps
at a sub-system level, adding a more meaningful physical picture to our observations.
But then the semi-classical models, in the present context, could not unambiguously
evaluate the effects of long-range interactions as reviewed in Sec.3.2.1. Also, the
Coulomb attraction experienced by the electron can not be eliminated in reality while
performing experiments. One might propose to perform attoclock experiment with a
hydride ion (\(H^-\)) to get rid of this problem, but this helium-like atom (structurally),
in addition to having a very low ionization potential, brings back the complication of
multi-electron systems. Interestingly, [120] used the very black-box of 3D-TDSE to
surpass this hurdle by remodelling the problem using a short-range Yukawa potential.
This thesis adopts such a scheme using which the contribution of tunnelling delays
to angular offsets are determined unambiguously.

5.2 Experimental set-up

The experiment broadly requires three main components: a laser that generates few-
cycle pulses, an atomic H source that serves as the target, and a REMI that observes
the tunnelling dynamics. A schematic of the experimental set-up is illustrated in Fig.(5.2). Detailed working of all the three are described in Chapter 3. However, in the following subsections we discuss the vacuum system that delivers the target into REMI and discuss the effect of CEP on attoclock.

5.2.1 Delivering H into REMI

The atomic H is produced using a RF discharge tube via electron impact as discussed in Chapter 3. One shall note that the high reactivity of H atoms can prove detrimental in creating a practical H atomic gas jet for our experiment. In order to avoid this, one shall make sure that the mean free-path length of the atoms is much higher than the characteristic dimension of the apparatus that is handling the gas jet. This would mean that the probability of atoms seeing each other is rarer than colliding with the walls of the apparatus. This regime of gas flow is referred to as the molecular flow regime. Such a beam source is generally characterised by a high gas reservoir, a small orifice to let the gas escape, various collimating apertures to shape the downstream flow and necessary pumping accessories to maintain a low pressure throughout the path. Such effusive beam techniques have been used over decades and the present discussion is no different from them.

The H gas produced using the discharge source acts as an effusive beam. The beam line then consists of two stages before it reaches the REMI: a source stage and a differential stage. Two pneumatic gate valves are used to separate the source, differential and REMI sections (see Fig. 5.2). Each stage is equipped with its own independent ion gauges and thermocouple gauges to read pressures. The source stage, that spans a length of ∼ 8 cm, holds the discharge tube which is constantly pumped out using a Turbo-molecular pump (Varian V-700 HT with a pumping speed of 700 l/sec for H₂) ‘backed’ by a high capacity rotary vane pump (Edwards E2M80 with 40 m³/hr displacement). This maintains the source stage pressure at < 10⁻⁶ mbar with no load but increases to ∼ 10⁻⁵ – 10⁻⁴ under gas load. Before it reaches the differential stage, the H beam passes between two deflector plates (of size 6 × 4 cm) used to remove any charged particles from the beam by applying a constant electric field of 26 V/cm. That electric field also serves to quench any metastable hydrogen atoms (mostly H 2s) produced during dissociation (see below in...
Figure 5.2: As part of the atomic beamline the water-cooled Pyrex discharge tube dissociating $\text{H}_2$ to H is driven with an optimized load of hydrogen gas ($\text{H}_2$), placed under a vacuum of $10^{-5}$ mbar in a source chamber. Any charged species coming from the jet are expelled using a uniform electric field before passing through an aperture to the next stage. A differential pumping stage, typically maintained at $10^{-7}$ mbar pressure, is employed to ensure no possible recombination of H atoms before they finally enter the REMI, commonly also known as ‘COLTRIMS’, through a 0.5 mm aperture as a supersonic jet. The few-cycle laser pulses then pass through a series of pellicle beamsplitters (used for varying the intensity) and ultra-broadband waveplates becoming elliptically polarized pulses that interact with H in the REMI. Fragments after the photoionization events accelerate in the uniform electric and magnetic fields of the REMI and finally get detected on the position sensitive detectors. The added information of position with TOF enables us to reconstruct the 3D MD of the fragments, soon after the interaction with the laser.
Figure 5.3: The H gas jet goes through 2 circular apertures of 4 mm and 0.5 mm as shown in (a) and (b), respectively. Two deflecting plates (6 × 4 cm) are attached just before the first aperture in order to remove any charged particles from the gas jet. The two apertures are automatically aligned as they are fixed into the centres of the flanges of the connected solid chambers. But in order to ensure that the open end of the discharge tube is aligned to these two apertures, we use a surveyor’s scope to look at the apertures from the discharge tube end while adjusting the position of the discharge tube with the help of micrometers as shown in (e) (see text for more details). Once aligned, the two apertures look as shown in (c) and (d). Light is illuminated at the end of the apertures in order to clearly see them and the photos are taken by an ordinary phone (at the end of surveyor’s scope’s eye piece) which caused the aberrations seen in the pictures.

The beam then passes through a 4 mm circular aperture into the differential stage, shown in Fig.5.3 (a). A pneumatic gate valve (Varian L8500304) is placed soon after the aperture which is convenient when baking these vacuum sections independently. The differential stage is maintained at a pressure of $< 10^{-8}$ mbar with the help of a turbomolecular pump (Pfeiffer TMU 521 Y P with a pumping speed of 520 l/sec) backed by a rotary vane pump (Pfeiffer Duo 10 M with 12 m$^3$/hr displacement). At the end of the differential stage, a second circular aperture of diameter 0.5 mm (see Fig.5.3 (b)) is placed through which the H atoms have to travel 45 cm to reach interaction region inside the REMI. The circular aperture is made by drilling a 0.5 mm hole in to a gasket connecting the differential stage to a second pneumatic gate valve (Varian SG0150PCCF). The differential stage, placed between the two gate valves is the shortest stage with length around 30 cm.

Both the source and differential stages are placed and supported on a mobile T-slotted aluminium framing, equipped with wheels. This structure is connected to
The atomic H gas jet is delivered into the REMI and made interacted with 30 fs linearly polarised (largely along Z direction) pulses. Figure 5.4 shows the TOF plot of the observed species in the REMI. The inset in (a) and (b) shows the observed signal of H\(^+\) in the TOF axis and the momentum plane \((P_x - P_z)\), respectively. X is the direction of gas jet and Z is the TOF axis. The dissociated and double ionised H\(^+\) with the same m/q is found along with the least energetic H\(^+\) from the atomic H. The kinetic energy release of double ionised H\(^+\) (identified by red arrows and font) is larger than the dissociated ones (identified in blue) due to the Coulomb explosion.

A nipple joining REMI with a flexible bellow. The two apertures are aligned directly to the interaction region by adjusting the height of the flexible bellow. However, prior to this, it is necessary to ensure that the central part of H gas jet goes through the apertures. This is achieved by ensuring the open end of the discharge tube is aligned with both the apertures. The discharge tube is held by a flexible bellow with 4 micrometers around it screwed into its flange, as shown in Fig.5.3 (e). The bellow is compressed and rests on the 4 micrometers under vacuum. By rotating the micrometers, one can align the position of the discharge tube in the bellow thereby aligning it with the apertures. While doing this, we use a surveyor’s scope, also known as automatic leveller (Leica Runner 24) to obtain line of sight through the discharge tube viewport, along the length of the apparatus and through the 0.5 mm pinhole aperture (see Fig.5.3 (c-d).

An initial check was performed letting the H gas jet interact with 30 fs pulses inside REMI. Upon its interaction with the laser pulse, the H\(^+\) signal was found as shown in Fig.5.4 and the driving pressure of H\(_2\) into the discharge tube was optimised.
to maximise the signal. The REMI chamber was not so clean as it was exposed to atmosphere during the process of integrating the H source to REMI, giving rise to a huge water peak ($\text{H}_2\text{O}^+$) in the TOF histogram (Fig.5.4 (c)). $\text{H}^+$ could also be identified in the momentum plane with X being the direction of gas jet and Z being the direction of TOF (Fig.5.4 (b)). The relatively least energetic $\text{H}^+$ is found at the centre of the histogram which is a characteristic feature of H ionisation, along with dissociated and double ionised $\text{H}^+$ (from $\text{H}_2$) on either sides.

**Detection of probable metastable H**

Given our scheme of producing H from electronic collisions from $\text{H}_2$, it is natural for one to expect the presence of a fraction of excited states of H. Most of those excited states will decay radiatively into 1s or 2s states within a few nanoseconds. The 2s state is metastable (its radiative one-photon transition to the ground state is forbidden by the selection rules) with a field-free lifetime of 1/7th of a second [160] determined by the rate of the two-photon transition. This is long enough to cover a distance of 1.6 m, with a typical speed of 2500m/sec for H, to reach the interaction region. This could possibly pose a problem in interpreting our results. However, the lifetime of this metastable state is shortened by an external electric field which couples 2s and 2p states, thus effectively quenching the 2s.

The lifetime of the 2s state of H as a function of external electric field E was calculated by Bethe and Salpeter [160] (Sec. 67 of the reference) and the theoretical formula was experimentally verified by Sellin [161]. That lifetime is given by,

$$\tau(E) = \tau(2p) \left\{ 1 + \frac{\delta^2}{[1 - \sqrt{1 + \delta^2}]^2} \right\} \quad \text{with} \quad \delta = \frac{2\sqrt{3}E\varepsilon_0}{L}, \quad (5.1)$$

where $\tau(2p)$ is the lifetime of the 2p state i.e. $\sim 1.6$ ns, $L$ is the Lamb shift (4.372 eV) and $a_0$ is the Bohr radius.

The H atoms produced in the discharge source travel through a 6 cm long deflector plates that has a field $\sim 26$ V/cm and also further 4 cm in a uniform DC field of 23 V/cm (22.8 V/cm to be precise, as 560 V is applied across 25 cm length) used inside the spectrometer. Estimating the population of metastables in the worst case scenario, we assume H to travel through 10 cm with uniform field of 22.8 V/cm.
Figure 5.5: (a) A 6 fsec linear polarised pulse having a Gaussian envelope (black line) with carrier-envelope offset phase 0 (red) and $\pi/2$ (blue). Their corresponding circular polarised pulses in the polarisation plane are shown in (b) and (c) using the same colour code, with the arrow pointing towards the $E_{\text{peak}}$. The black circle in (b)-(c) is the polarisation ellipse in and also happens to be the locus of the peak field, when CEP is not stabilised.

From the Eqn.(5.1), the lifetime of H $2s$ for the electric field of 22.8 V/cm was calculated to be less than 700 ns. Considering the typical beam velocity of 2500 m/s, hydrogen atoms will travel $(700 \text{ ns} \times 2500 \text{ m/s} = 1.75 \text{ mm})$ less than 2 mm during H $2s$ lifetime. Hence, we can safely assume that for every 2 mm that the H atoms pass, the H $2s$ population would be reduced to a fraction of $1/e$ along the way. As the atoms need to cover 10 cm (100 mm) through the electric field (6 cm between the deflector plates and 4 cm inside the spectrometer) to reach the laser focus, the population of H $2s$ will be reduced to at least $\left(\frac{1}{e}\right)^{100/2} e^{-50}$ or to a fraction of $10^{-22}$ to essentially zero.

5.2.2 Elliptically polarised light for ‘Attoclock’

We generate 6 fs pulses (FWHM in intensity with Gaussian envelope shown in Fig.5.5) around 770 nm central wavelength from the commercially available FEMTOPOWER Compact Pro CE-Phase laser system that has a repetition rate of 1 kHz. Although the angular streaking works best with circularly polarized few-cycle pulses, there is an experimental issue with determining the angle at which the electric field (and related to it tunnelling ionization probability) reaches its maximum. That angle depends on the CEP of such pulses. Presently, the best stabilization techniques achieve CEP noise of about 100-150 mrad, corresponding to about $7^\circ$ or 50 attoseconds uncertainty in angle/time measurement, which is already comparable to, or exceeds
the expected tunnelling times. And in the case of no CEP stabilisation, the peak field of the circular-polarised pulse is uniformly distributed in the polarisation plane, giving us no information on the angle of maximal field whatsoever. However, this experimental issue is resolved by using slightly elliptically polarized light pulses. Even for an ellipticity of 0.88 (very close to circular) without CEP stabilization, the electric field will reach its maximum when it points along the major axis of the polarization ellipse, and the direction of the electric field can be determined with high precision using basic polarimetry [106]. In the following thesis an ellipticity of 0.84±0.01 was used. We used phase retarders to introduce the desired ellipticity, $\epsilon$ with a desired orientation of the polarisation ellipse. The ellipticity $\epsilon$ is defined as the ratio of minor axis to the major axis in field, i.e. $E_x/E_y$. The field for such a pulse with Gaussian envelope $G(\tau)$ can be expressed as:

$$\vec{E}(t) = G(t) \left[ \frac{\epsilon}{\sqrt{1 + \epsilon^2}} \cos(\omega t)\hat{x} - \frac{1}{\sqrt{1 + \epsilon^2}} \sin(\omega t)\hat{y} \right],$$

(5.2)

$$G(t) = \exp \left[ -2\ln(2) \left( \frac{t}{\tau} \right)^2 \right].$$

(5.3)

Here $\tau$ correspond to the FWHM of the pulse when expressed in intensity. Hence, when no CEP stabilisation is performed, the maximal field is around the major axis of the polarisation ellipse, as shown in Fig.5.6. Therefore by measuring the ellipticity and the orientation of the polarisation ellipse, information regarding the major axis and thereby the maximal field is inferred. This would imply two positions of maxima in the PMD too, but around the minor axis. Also that in the current experiment, the atomic beam diameter is half the Rayleigh range of the focal spot in REMI. This would mean that the CEP changes across the focal spot along the beam propagation. However, since CEP stabilisation is not performed, the averaging of Gouy phase occurs naturally while comparing experimental data with CEP-averaged momentum spectra from numerical simulations.

### 5.3 Data acquisition and analysis

The experimental procedure can broadly be described in the following steps and would be discussed in detail thereafter.
Figure 5.6: Parametric plots of a 0.84 elliptic polarised light shown as a function of CEP increasing from 0 to $7\pi/4$ in steps of $\pi/4$ (from left to right 0-3$\pi/4$ on top and $\pi - 7\pi/4$ in the bottom). The black arrows point the direction of maximal field. The outer black dotted line correspond to the locus of maximal field for a circular polarised field with a random CEP. In case of 0.84 as ellipticity, a maximum angular deviation of $\sim 2.5^\circ$ occur away from the major axis. However as CEP gets randomised, the effective maxima is located along the major axis.

1. Generate bandwidth limited few-cycle pulses from the laser (this includes characterising the pulse using an intensity-interferometric autocorrelator as discussed in Chapter 3.).

2. Introduce a known ellipticity and perform optical polarimetry that includes characterising the polarisation ellipse in the analyser’s (a linear polariser) frame of reference.

3. Transfer the analyser’s frame of reference to REMI’s coordinate system.

4. Perform a similar polarimetry measurement but in the REMI’s frame of reference using atomic H ion yield.

5. Acquire streaking data at various intensities using pellicle beam splitters.

**Bandwidth limited pulses**

Few-cycle femtosecond pulses are generated from the commercially available laser system, FEMTOPOWER Compact pro CEPPhase. Fused silica wedges are used to com-
Figure 5.7: An illustration of how optical polarimetry is performed, wherein a quarterwave plate (with the combination of halfwave plate not shown in the figure) generates elliptic polarised light. A linear polariser/analyser followed by a power meter is used to measure the power as a function of polariser’s optic axis’ orientation. The Fig.5.8 shows such measurements in case of linear, circular and elliptic polarised light.

pensate the chirp and achieve bandwidth-limited pulses. An intensity-interferometric autocorrelator arranged in a Mach-Zender architecture is used to characterise these pulses. We use the kinetic energy release of the $\text{H}^+$ yield from the ionisation channels of $\text{H}_2$ to achieve the same inside REMI. A detailed discussion on these can be found in Chapter 3.

**Optical polarimetry**

The 6 fsec linear polarised pulses go through a quarter-wave plate (QWP) and a half-wave plate (HWP) that introduce ellipticity and orient ellipse in a desired direction respectively. These waveplates are made using birefringent material that possess different refractive indices for parallel and perpendicular polarised components of light. The direction along which the refractive index is low/high is called the fast/slow axis respectively. As a result, this introduces a phase delay between the vertical and horizontal component of polarisations altering the final state. By choosing an appropriate thickness as in the case of a quarter and half wave plates, they can be used to introduce ellipticity or orient the polarisation direction. A complete description of such an elliptic polarised light is possible using Mueller-Stokes calculus [162]. Using this it can be shown that light incident on a HWP at an angle $\alpha$ with respect to the fast axis rotates its polarisation by $2\alpha$, without introducing any ellipticity. On the contrary, QWP turns a linear polarised light to a perfect circular polarised light (with $\epsilon = 1$) when it sees a fast axis at $\pm45^\circ$ angle and leaves it unaltered at $0^\circ$ or $\pm90^\circ$. Any other angle leads to an elliptic polarised light. In
terms of a transformation matrix, the action of a HWP and a QWP on a linear polarised light at angle $\theta$ w.r.to fast axis can be expressed as:

$$T_\delta(\theta) = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos^2(2\theta) + \cos(\delta) \sin^2(2\theta) & \cos(2\theta) \sin(2\theta)(1 - \cos(\delta)) & \sin(2\theta) \sin(\delta) \\ 0 & \cos(2\theta) \sin(2\theta)(1 - \cos(\delta)) & \cos(\delta) \cos^2(2\theta) + \sin^2(2\theta) & -\cos(2\theta) \sin(\delta) \\ 0 & -\sin(2\theta) \sin(\delta) & \cos(2\theta) \sin(\delta) & \cos(\delta) \end{bmatrix}. \tag{5.4}$$

Here $\delta$ is the phase delay introduced between the components passing through fast and slow axis. For a HWP, it is $\pi$ and $\pi/2$ for a QWP. However to characterise the polarisation ellipse, leaving its helicity i.e. right or left handedness, one can perform a simple optical polarimetry measurement. This is done with the help of a linear polariser. Linear polarisers are dichroic in nature, wherein they selectively transmit polarisation component that are aligned with its characteristic optic axis. Hence, by measuring the transmittance of light through the polariser as a function of the optic axis orientation, one can identify the polarisation of incident light (see Fig.5.7).

Let us consider a polarisation ellipse with semi-major axis $a$, semi-minor axis $b$...
and an azimuthal angle $\phi$ as shown in Fig.5.8. We can then measure the transmitted field passing through a polariser as a function of the optic axis’ orientation $\theta_{\text{pol}}$. However it is easy and a common practice to measure power in the lab and hence this is proportional to the intensity. A power meter (Thorlabs PM310D) was used in the experiment to perform polarimetry to measure the ellipticity and orientation of the polarisation ellipse as shown in Fig.5.8. The transmitted intensity (power) from the measurement can then be fitted using the function [163],

$$I(\theta_{\text{pol}}) = a^2 \cos^2(\theta_{\text{pol}} - \phi) + b^2 \sin^2(\theta_{\text{pol}} - \phi).$$  \hspace{1cm} (5.5)

Here $b/a$ gives the ellipticity, manifested as the modulation depth, while $\phi$ gives the angle at which the polarization ellipse, i.e. the major axis, was oriented. The ellipticity is defined as $\epsilon = \text{major axis/minor axis}$ (of the E field), such that it spans the range from 0 to 1 corresponding to linear and circular polarization, respectively. Figure.5.8 shows plots of circular (shown in red color), linear (black curve) and elliptic (blue curve) measured in the lab. The maximum and minimum ellipticity were found to be 0.97 and 0.18 identified as circular and linear polarised light, respectively. They are away from the perfect values of 1 and 0 which can be attributed to the imperfect response of the polariser for an ultra-broadband spectrum of wavelengths, and unaccounted systematic offsets in polariser angle and power meter readings. The blue curve representing elliptic polarised light of $\epsilon = 0.84$ is used for the attoclock experimental data. Although $\phi$ can be inferred from the optical polarimetry data, we shall measure it in the atom-light interaction reference frame. This requires calibration of the polariser’s optics axis in REMI’s frame of reference, discussed in the following section.

**Determining polarisation ellipse in the calibrated reference frame**

In order to find the first marker for measuring the tunnelling delay i.e. the maximal field, we perform polarimetry using atomic H ion yields. Given the highly non-linear dependence of the ionization probability as a function of the electric field, this mechanism provides a more accurate determination of the polarization ellipse for day-to-day measurements. The angular offset is defined as the angular difference in the direction of most probable photoelectrons emitted and that of the maximum
Figure 5.9: The elliptically polarized few-cycle pulse is passed through a polarizer, with its optical axis aligned to the reading $90^\circ$ on it, which makes it linear, and interacts with the atomic jet inside the REMI. The resulting PMD is shown in (a). (b) The PMD in the polarization plane is then plotted as a function of streaking angle. The orientation of the field is found by determining the peaks of the distribution, thereby giving us a relative offset between the frames of the polarizer and the REMI. The polarization is chosen parallel (in this case vertical) to the time-of-flight axis due to better momentum resolution. An offset of $\sim 3^\circ$ was measured and used to calibrate our measured offsets and polarimetry. (c) Using these calibrated angle, polarimetry is performed using $\text{H}^+$ yields as shown in (c). The non-linearity of the ionisation rate w.r.t. intensity provided an accurate determination of major axis.

The field. However, the maximal field is determined using polarimetry in the polariser’s reference frame and the PMD is measured in REMIs frame of reference. In order to have an absolute comparison of the measured angles in the polarization measurement and the angular distributions, we use a polariser to convert the laser pulse into linear polarization before sending it into REMI to ionize atomic H. Since with a linearly polarized field, the electrons mainly emit along the laser polarization axis, which is parallel to the polariser’s optical axis (see Fig.5.9 (a)), we calibrate the angle of the polariser’s optic axis with the angle of the peak PMD measured in the REMI’s coordinate system (Fig.5.9(b)).

The projected PMD in the polarization plane ($P_x - P_z$) is divided into optimal polar angular bins $\Delta \theta$, where $\theta$ defined as $\tan^{-1}(P_z/P_x)$, is the streaking angle. The distribution acquired by radially integrating the counts in each bin, $f(\theta)$, is plotted against the streaking angle and is then fitted using a double Gaussian function of
the form:
\[ f(\theta) = \sum_{i=1}^{2} a_i e^{\left(\frac{\theta - b_i}{c_i}\right)^2} \] (5.6)

using a least-square fitting routine that is available in MATLAB R2015a. The values of \( b_i \)'s give the direction of most probable ejection. The routine provides a 95% (2\( \sigma \)) level confidence bounds of the fit from which the standard error is calculated. The peak angle of the PMD is extracted using the above described double Gaussian fit routine and a relative offset of \( \theta_{sys} = b_i - 90^\circ \) with an error of \( \delta\theta_{sys} \) between the two coordinate systems is determined. This enabled us to work in the same frame of reference such that the relation is \( \theta = \theta_{pol} - \theta_{sys} \), where \( \theta_{pol} \) is the angle of the polariser’s optic axis.

We then determined the orientation of polarisation ellipse in this calibrated frame by performing a polarimetry measurement using atomic H ion yields (see Fig.5.9 (c)). In order to account for the non-linear nature of the ionisation probability, we used the fit function \( e^{-I(\theta)} \), with \( I(\theta) \) given in Eqn.(5.5). Using a similar least square fitting routine we infer the orientation of ellipse \( \theta_{ellipse} \) with a standard error of \( \delta\theta_{fit} \). However the error in determining the relative offset accumulates to this fit giving us
\[ \delta\theta_{ellipse} = \sqrt{\delta\theta^2_{fit} + \delta\theta^2_{sys}}. \] (5.7)

**Data acquisition and extracting offsets**

Once the polarisation ellipse is defined, the elliptic polarised pulse streaks the hydrogen atoms entering the REMI. The law of conservation of momentum ensures that the streaking momentum of electron and proton is same. However, we choose to observe and analyse the MD of electrons, which displays a better resolution due to its lighter mass. To make certain that we pick electrons from H and not from any other species like H\(_2\), H\(_2\)O etc., we measure the proton and electrons in coincidence. It is necessary to detect \(< 1 \) ionisation event per laser shot so to reduce the rate of false coincidences. Cobold PC 2011 R3 software that works in conjunction with REMI can help us monitor this by producing histograms as shown in Fig.5.10. It can be seen that the 0 electron-0 ion dominates most of the time, meaning we have an average of less than unity atom/molecule being ionised per laser shot. The experiment performed in fact had a probability of \(< 4\% \) of false coincidences.
Figure 5.10: Shows the number of ions vs electrons detected per laser shot in the experiment data that was acquired at an intensity of $1.65 \times 10^{14}$ W/cm$^2$. The counts are shown in logarithmic scale and the number of events with no counts are dominating which is an indication of an average number of < 1 ionisation events occurring per laser pulse. This ensures a very low rate of false coincidences in our measurement of electrons from the H.

The intensity range spanning the tunnelling regime in H is so low that we had to reduce the power by 70%. This was achieved by using a couple of coated pellicle beam splitters (Thorlabs BP145B2) that has a maximum reflectance of 45%. Although the coating works predominantly in the region of 700-900 nm (covering the central wavelength of 770 nm), it did not have a considerable effect on the pulse duration and the orientation of the ellipse, beyond the errorbar. The intensity is varied using a series of pellicle beam splitters thereafter (Thorlabs BP108) that has a maximum reflectance of 8% in the wavelength region of 400nm to 2400 nm. All the beam splitters are made of a 2 $\mu$m nitrocellulose membrane with a refractive index of 1.5 at 550 nm. A quick check was done in order to ensure that such a thickness had no effect on the dispersion of the pulse. The lowest possible intensity where a considerable amount of counts in REMI obtained was 4.6 mW corresponding to $1.65 \times 10^{14}$ W/cm$^2$, with a value of $\gamma = 1.12$.

Ions and electrons detected in the REMI are later analysed by application of a coincidence filter. This includes first selecting a narrow time window in TOF of species...
Figure 5.11: A figure illustrating the application of coincidence filters on the H and its effect on the PMD acquired at a peak intensity of \(1.95 \times 10^{14}\) W/cm\(^2\). The top row shows the detected ion and electron species in a TOF and PMD spectra. The first peak corresponds to \(\text{H}^+\) from H, the second one is \(\text{H}_2^+\) and the third broad peak is the background water peak. The bottom row shows these spectra post application of the coincidence filters.

that correspond to H (see Fig.5.11). Once the TOF filter is applied we consider the ionisation events in which only one H ion is detected. We then look for a subset of those events in which a single electron is simultaneously detected in the same ionisation event. This ensures that the electron-proton pair originates from the same H atom. The number of electron-proton pairs that passes through the coincidence filters is only 10-14% of the total electrons that are acquired. The PMD generated this way is used for extracting angular offsets as shown at the right bottom of the Fig.5.11.

Extreme care was taken in calculating and generating these 3D-MD from the raw
Figure 5.12: (a) Shows a radially symmetric PMD generated using 3D-TDSE code for H at a peak intensity of $1.95 \times 10^{14} \text{ W/cm}^2$, with an ellipticity of 0.84 and averaged at 8 different CEP values from $[0, 2\pi]$ in steps of $\pi/4$. Below is the experimental data acquired at the same intensity with H with its origin shifted by $\sim 0.032$ a.u. (b) Shows the corrected PMD plotted in polar plot with X axis being the angle defined as $\tan^{-1}(P_z/P_x)$ and Y axis is $P = \sqrt{P_x^2 + P_z^2}$. The polar plot is rotated by $\sim -75^\circ$ to confine the lobes onto either side of the X-axis as shown in the below subplot. (c) Shows the overlap of kinetic energy of each lobe (in red and blue curves) calculated by integrating the rotated PMD radially. The below subplot shows the residuals at each point, quantifying the goodness of the overlap. A good overlap was achieved by shifting the origin from (0,0) to (0.01,0.03) and the relative shift among the peaks of both the lobes was found to be zero.

data. Of all, one important thing is calibrating the B-field and E-field that is applied along the spectrometer. As described in Chapter 3, we achieve this by acquiring data at a very low E-field causing the electrons to spiral down to the detector with its cyclotron frequency. By using basic Newtonian dynamics with the radius and spacing between the cycles and TOF, one can infer E and B-fields. Although we determine this to an accuracy of 1 in 1000 parts, there can always be a margin of error. This error shows itself as a displacement of the whole PMD from the origin. The streaking angle in the polarisation plane $P_x - P_z$ is defined as $\tan^{-1}(P_z/P_x)$. Therefore an error in its centroid position can yield wrong angular offsets. In order to correct such an error, the lobes are individually separated in polar coordinates and the corresponding kinetic energy is plotted (see Fig.5.12(b)-(c)). In the ideal case of no CEP stabilisation, one should expect the lobes to be radially symmetrical as shown in Fig.5.12 (a). We then introduce a shift in the origin accordingly, by taking the overlap of the kinetic energy curves of these two lobes as feedback.
Figure 5.13: The presented data are for a peak intensity of $1.95 \times 10^{14}$ W/cm$^2$. The major axis of the polarization ellipse defines the direction of the peak electric field and can be determined by basic polarimetry after careful calibration as described in sec. 5.3. (a) Experimental data for the PMD in the polarization plane. A corresponds to the peak electric field and B & C are the expected and measured peaks of PMD in the polarization plane. (b) (Top) The cumulative photoelectron signal in the polar angular bins of 2 degrees each in the polarization plane. A double Gaussian function as in Eqn.(5.6) is fitted to determine the position of each peak. (Bottom) Atomic H-ion yield data as a function of calibrated polariser angle $\theta$ is fitted using the function $e^{-I(\theta_{pol})}$ with $I(\theta)$ defined in Eqn.(5.5) to determine the major axis of the polarization ellipse. The errors in the fit are determined by the confidence bounds of the various fit parameters involved in the fit function and the error in angular offsets are calculated using Eqn.(5.9). The points A, B, C in (a) are also shown in (b) to illustrate the measured angular offsets. The angular difference of $10.87^\circ \pm 1.42^\circ$ between B and C is the measured angular offset.

This was then followed with the double Gaussian fitting routine as described above in Eqn.(5.6). The Gaussian peak $\theta_{streak}$ gives us the asymptotic angle of the most probable electron trajectory, with an error of $\delta \theta_{streak}$. Having both the measurements, polarisation ellipse and peak of PMD, precisely taken in the same frame of reference enables the angular offset and its corresponding error to be determined via,

$$\theta_{offset} = \theta_{streak} - \theta_{ellipse} - 90^\circ$$

$$\delta \theta_{offset} = \sqrt{\delta \theta_{streak}^2 + \delta \theta_{ellipse}^2}.$$  

The systematic offset corrected in the data was always < 0.05 a.u. in each axis,
which could at maximum give rise to a 1° error (found through fitting routine). Since these are systematic errors rather than random errors, they are not considered in Eqn.(5.9).

5.4 Results and discussion

5.4.1 Central idea in determining tunnelling times

In order to determine the tunnelling delays unambiguously, we first compare our results with the full solutions of *ab initio* 3D-TDSE calculated accurately within the non-relativistic framework using the electric dipole approximation, that generate PMD projected on the polarization plane with the same pulse parameters as were used in the experiments. Once a good agreement is found, we then use the same numerical codes solving 3D-TDSE to artificially eliminate the parent ion-electron attraction by choosing a short-range attractive potential. [120]. The short range potential used is the Yukawa potential that binds the electron to proton, in such a way that the ground state energy of H atom is retained i.e. 13.6 eV as shown in Fig.5.14. It is of the form,

\[ V(r) = -\frac{Z}{r}e^{-r/a} \text{ where } Z = 1.908 \text{ & } a=1. \]  

(5.10)

Therefore any offsets observed in the PMD generated by Yukawa potential would mean a real tunnelling time of the electron. Although, previous theoretical work in which such a scheme was proposed [120] showed zero offsets, they only solved a model problem with an unrealistic pulse with the field \( E(t) = -\frac{\partial A(t)}{\partial t} \), where \( A(t) = -A_0 \cos^4(\omega t/4) [\cos(\omega t)\hat{x} + \sin(\omega t)\hat{y}] \). Also, it was followed by a later work [121] predicting non-zero tunnelling times. Of all the estimated tunnelling times, Larmor time was claimed to be the right choice for the attoclock scenario and was also found to be the least around \( \sim 100 \) as at a field strength 0.02 a.u. and monotonously decreasing to \(< 10 \) as at a field strength of 0.14 a.u.. Therefore it is required of us to verify and validate these predictions experimentally.
Figure 5.14: Potential curves depicting the cases of both Coulomb potential (blue dot-dashed curve) given by $V(r) = -1/r$ and a short range Yukawa potential (red thick curve) given by $V(r) = Z/r e^{-r/a}$ in which the electron is bound to a proton with the same binding energy as -13.6 eV or -0.5 a.u.

### 5.4.2 Numerical simulations

The *ab initio* numerical simulations of 3D-TDSE are provided by two theoretical groups for this project: one by Prof. Klaus Bartschat’s and Dr. Nicolas, Douguet (currently at University of Florida) from Drake university and the other by Prof. Anatoli Kheifets group that includes Alexander Bray and Dr. Igor Ivanov (currently at IBS, South Korea). The two independent numerical codes employed by two groups to solve 3D-TDSE are conceptually similar, both relying on spherical-harmonics expansions of the wave-function to represent its dependence on the angular variables and treating the radial variable by discretizing the TDSE on a grid. Both groups used the Matrix Iteration Method to propagate the TDSE in time. Detailed descriptions of the numerical techniques used by the two groups can be found in [164,165]. Careful checks were performed to ensure that convergence with respect to the parameters defining the accuracy of the calculation (e.g., the number of partial waves in the expansion as well as the step sizes on the space-time grid) was achieved. For the peak intensity of $1.65 \times 10^{14} \text{ W/cm}^2$, the results from the two groups were compared to ensure that the independent implementations of the computational techniques gave same results within the error bar due to the uncertainty of the fitting procedure used to determine the angular offset. The maximum orbital angular momentum
$l_{max}$ needed in the partial-wave expansion was 40 for $1.4 \times 10^{14}$ W/cm$^2$ and 100 for $3.9 \times 10^{14}$ W/cm$^2$, respectively. Specifically, the components of the vector potential $\vec{A}(t)$ for a pulse with ellipticity $\epsilon$ were set as:

\[
A_x(t) = -\frac{E_0}{\omega} G(t) \frac{\epsilon}{\sqrt{1 + \epsilon^2}} \cos(\omega t + \phi), \tag{5.11}
\]

\[
A_z(t) = -\frac{E_0}{\omega} G(t) \frac{1}{\sqrt{1 + \epsilon^2}} \sin(\omega t + \phi), \tag{5.12}
\]

\[
A_y(t) = 0. \tag{5.13}
\]

The envelope function $G(t)$ was a Gaussian ramped on and off over three optical cycles each, respectively such that the FWHM was 6 fs in intensity. The electric field was obtained as $\vec{E}(t) = -\frac{d\vec{A}(t)}{dt}$. Finally, the CEP $\phi$ was varied in steps of $\pi/4$ from 0 to $2\pi$ and the results were averaged.

### 5.4.3 Results

The peak intensity of the laser pulses was varied from $1.65 \times 10^{14}$ W/cm$^2$ to $3.9 \times 10^{14}$ W/cm$^2$. The angular offsets were extracted from our experimental data as described in the above section. These attoclock observables from the experiment are directly compared to the \textit{ab initio} simulations provided by two independent theoretical groups. The calculated momentum spectra were then analysed using the same methods as in the case of their experimental counterparts. The error bars associated with the theoretical data are due to uncertainties in the double Gaussian fitting procedure used to determine the angular offsets.

The experimental results are in an excellent agreement with those of the theoretically simulations (shown as circles in Fig.5.15) from the two independent groups, which are also in mutual agreement. We see the expected trend of the angular offset decreasing as the field strength increases as shown with black diamonds in Fig.5.15. This was a feature previously explained with the argument that the tunnelling time decreases due to decrease in the barrier height and width with increasing intensity. However in order to segregate the real tunnelling delays from the Coulomb drag which can also give rise to angular offsets, simulations using the short-range Yukawa potential with the same experimental pulse parameters were performed. The computations with the Yukawa potential show a zero angular offset (within our
Figure 5.15: The experimental observations are compared to *ab initio* 3D-TDSE simulations with both Coulomb potentials, provided by two independent groups marked as 1 and 2. To disentangle the effects of the Coulomb potential on the continuum electron, we also include the 3D-TDSE simulations for a Yukawa potential. The same extraction procedure was used to determine the offset angles from experimental results and theoretical simulations for both Coulomb and Yukawa potentials. Our numerical experiment demonstrates that the observed angular offsets are entirely due to the electron scattering by the long-range Coulomb potential of the ion.

Numerical and fitting uncertainty) for all intensities (triangles in Fig. 5.15). That leads to the definitive conclusion that for atomic H attoclock the offset angles originate entirely from the Coulomb scattering of the ejected electron with no contribution from any tunnelling delay. Consequently, our results are consistent with zero time delay between the peak of the electric field and the appearance time of the continuum electron measured by the attoclock, corresponding to instantaneous tunnelling.

Based on our estimated experimental and numerical uncertainties we can put an upper bound on the tunnelling time delays by considering the angular offset, in the case of the Yukawa potential, that has deviated from the zero reference line the most. We estimate that the angular offset cannot exceed 0.25° for the Yukawa potential, which corresponds to the maximum possible tunnelling time delay of 1.8 attoseconds. This is substantially less than values of any commonly used theoretical definitions of tunnelling times as predicted in [121] for H. Thus one can effectively rule out all
of these tunnelling times from being interpreted as the time taken by the particle
to tunnel through the barrier, especially in the context of strong field ionisation. It
is also likely that any experimental search for a finite tunnelling time will have to
explore the zeptosecond ($10^{-21}$ s) time domain.

5.5 Summary

A brief introduction of attoclock experiment was discussed explaining the motivation
for performing it with H. A discussion on the construction of an atomic H beam
line was presented, followed by a detailed description of the experimental set-up and
analysis of extracting angular offsets. Finally, through both precise measurements and
high-accuracy ab-initio simulations, properly validated by mutual comparison, the
issue of any possible tunnelling delays was addressed meaningfully and unambiguously
by our study. We anticipate our results to have strong implications, as we have
completely excluded the issues of multi-electron effects that were present in other
experiments. High-precision experiments with a benchmark system such as H
open the way towards accurate measurements of photoionization delays for various
multi-electron atoms and molecules. Those measurements will provide important
information on their specific electron dynamics, in particular on electron-electron
correlations. Therefore, future measurements of tunnelling delay times with greater
accuracy in zeptosecond domain may reveal more interesting features.
Attoclock studies on dissociative dynamics of $\text{H}_2$

6.1 Introduction

The current chapter deals with the recent studies undertaken in understanding the dissociative dynamics of molecular hydrogen ($\text{H}_2$). Much alike atomic hydrogen, $\text{H}_2$ (and its isotopes) serves as a molecular benchmarking system. Given its chemical composition made of the simplest atoms, it can be fully investigated in theory and at the same time, unlike atomic H, it is easily accessible for experiments. It is also the simplest molecule for quantum mechanically describing the effects of correlated electrons and nuclei. Further, it is considered as a benchmarking species in studying isotopic effects—no other molecule has an isotope double its mass that is also available in abundance.

On the flip side, modelling photo-molecular processes is challenging due to the complexity involved in accounting for various degrees of freedom that the molecule possesses like rotational, vibrational and electronic degrees of freedom. The pivotal factor that is taken into consideration in either including or excluding these degrees of freedom lies in the timescales that are of interest. Rotational degrees of freedom play a role on the timescales of picoseconds ($1\ \text{ps} = 10^{-12}\ \text{s}$) while the vibrational and electronic dynamics occur at femtosecond ($1\ \text{fs} = 10^{-15}\ \text{s}$) and attosecond ($1\ \text{as} = 10^{-18}\ \text{s}$) timescales, respectively. With the availability of lasers spanning from picoseconds to attoseconds, it is now possible for us to image molecular dynamics in real time using well-known pump-probe techniques.

A pump-probe technique generally involves two laser pulses, wherein the first pulse triggers the molecular reaction and the second pulse probes the initiated dynamics. This is done by introducing a variable delay between the two pulses and
in a systematic way recording the photo-molecular processes much the same as a film. Studies of this kind have been successfully performed in the past to observe vibrational, rotational and electronic dynamics in molecules. This chapter presents some results of such an attempt in understanding the dissociation dynamics of \( \text{H}_2 \), albeit using the attoclock technique in a novel way by looking at the momentum distribution (SF-MFPMD), where only a single pulse is used.

The first section presents a brief introduction to the strong-field ionisation of \( \text{H}_2 \) and its dissociation channels. The second section presents the experimental procedure and set-up. The third sections presents the analysis of these acquired data and finally the results are presented. Later, we present a summary of the chapter in the fifth section.

### 6.2 \( \text{H}_2 \) in strong fields

Hydrogen molecule, like any other molecule or atom, undergoes strong-field ionisation through tunnelling mechanism. However, the presence of two central cores/nuclei binding the valence electrons introduces an extra parameter i.e. inter-nuclear distance which complicates the study of its dynamics. In contrast to hydrogen atom, the hydrogen molecule possesses extra degrees of freedom in the form of vibrations and rotations. These extra degrees of freedom also play a role in influencing the strong-field ionisation that can lead to either ionisation pathways or dissociative pathways and conversely can be used in a controlled manner to steer the ionised/bound electron wavepacket in a desired way.

Hydrogen may be singly ionised as \( \text{H}_2 \rightarrow \text{H}_2^+ + e^- \), leading to either a gerade \((1s\sigma_g)\) or ungerade \((2p\sigma_u)\) state. Gerade state is a stable bound state of \( \text{H}_2^+ \) that can be in any of the vibrational state (red curve in Fig.6.1 (a)), while the ungerade state (blue curve in Fig.6.1 (a)) is unstable and dissociates into a proton and H, \( \text{H}_2^+ \rightarrow \text{H} + \text{H}^+ \). The hydrogen molecule also can get doubly ionised (black curve in Fig.6.1 (a)), which eventually due to Coulomb repulsion will explode into two protons, \( \text{H}_2 \rightarrow \text{H}_2^{2+} + 2e^- \rightarrow 2\text{H}^+ + 2e^- \). The information on the pathway is encoded into the kinetic energy of the fragments \([166]\). The energy can also act as an indicator for the inter-nuclear separation \((R)\). The ionisation rate is enhanced when
Figure 6.1: (a) Shows the potential curve for molecular hydrogen showing different pathways of ionisation. Adopted from [169]. (b) Shows the MD of H\(^{+}\) ion fragments in the polarisation plane detected in REMI when ionised using linear polarised light. Various pathways of fragmentation can be observed depending on the kinetic energy \(\propto |p|\) of the ions, such that the Coulomb exploded H\(^{+}\) have the highest kinetic energy, followed by the enhanced ionisation ions and the dissociated H\(^{+}\) ions have least energy.

The inter-nuclear separation is larger and the energy of the protons detected are lower than those from the Coulomb exploded doubly ionised channel [167], occurring at equilibrium distance. Such \(R\)-dependent ionisation is commonly known as enhanced ionisation [168]. We can differentiate these channels in the MD of the protons in the laser polarisation plane using REMI as shown in Fig.6.1 (b).

The degrees of freedom that the molecule possesses can also be distinguished as nuclear and electronic. Typical nuclear dynamics occur at fs to ps timescales, while the electronic rearrangements happen at sub-femtosecond timescales. This is theoretically modelled using Born-Oppenheimer approximation while performing numerical simulations to solve TDSE. The approximation treats nuclear and electronic dynamics separately wherein a nuclear part of the wavefunction encodes the rotational and vibrational dynamics with the electronic part describing the electronic state. In addition, when molecules interact with ultrashort pulses (< 100 fs), few models approximate the field to only influence the electronic motion and hence the nuclei are considered static. This is commonly referred to as the ‘frozen nuclei approximation’. 
CHAPTER 6. ATTOCLOCK STUDIES ON DISSOCIATIVE DYNAMICS OF H$_2$

6.2.1 Laser induced alignment/orientation of the molecules

Molecules in gas phase are generally randomly oriented. An ensemble of molecules are said to be ‘aligned’ when their molecular axes are fixed in space. When speaking of heteronuclear diatomic molecules, aligning without inversion symmetry can lead to ‘orientation’ (see Fig. 6.2). Laser induced alignment is widely studied theoretically and experimentally since mid 90’s [170]. Semi-classically, depending on the molecular polarizability tensor, the external laser field can distort the electron distribution, thus inducing a dipole moment. Given a linearly polarised strong non-resonant optical field, it interacts with the induced dipole and in an attempt to minimize the energy, the system tends to generally align along the direction of the polarisation.

Quantum mechanically, a strong pulse with sufficient bandwidth can populate multiple rotational levels $J$ such that the wavepackets are tightly aligned in its conjugate space, $\theta$ [171]. The same could also be achieved in 3 dimensional space wherein an elliptically polarised field is used to confine a diatomic molecule’s movement in the polarisation plane. This technique is known as adiabatic alignment, due to the usage of pulses with pulse durations much longer than that of the typical rotational timescales of the molecules (picoseconds).

By using pulses as short as $<\text{ps}$ it was shown theoretically [172] and later experimentally [173], that the molecule can be dynamically aligned in a field-free environment. This could be understood as the short pulse imparting a ‘kick’ to the molecule transferring angular momentum to it. This leads to a Raman excitation process eventually creating a ground-state rotational wavepacket that makes the molecule aligned after every time interval $T_{\text{rev}}$, known as the revival time. The first alignment dependent strong-field ionisation study of a neutral molecule was demonstrated using N$_2$ [174].
6.3 Motivation for attoclock on H$_2$

We would like to study molecular dynamics of H$_2$ using the attoclock technique. As mentioned, the loss of spherical symmetry unlike atomic H and the orientation of the molecule could possibly affect the electron wavepacket with regards to how it interacts with external field post ionisation [175]. Therefore, we would like to study H$_2$ with the tool of attoclock based on its orientation, in its own molecular frame. Please note that in case of H$_2$ the terms ‘alignment’ and ‘orientation’ means the same and hence we use them interchangeably.

6.3.1 Why alignment dependent studies using H$_2$?

Initial studies using N$_2$ [174] found that the ionisation rate of the molecules aligned parallel to the polarisation direction is $\sim 4$ times higher than the perpendicular ones. Similar theoretical studies were undertaken on hydrogen using \textit{ab initio} non-adiabatic quantum molecular dynamics simulations [176], TDSE considering 2 electrons but with frozen nuclei approximation [177] and later including vibrational dynamics [178], SFA [179] etc. It was also found that in case of H$_2$ the electron emission angle is favoured for $\theta = 0^\circ$, with $\theta$ being the angle between the molecular axis and laser polarisation [177]. However, a similar experimental study when done on CO$_2$ in addition to N$_2$ and O$_2$, resulted in a $\theta = 45^\circ$ [180]. Hence, it is now established that the ionization of the molecule has strong dependence on the symmetry of the initial electronic state and the orientation of the molecule [175].

In addition to it, the ionisation forms an important and primary step for many strong-field processes like HHG, non-sequential double ionisation (NSDI), ATI etc. Given that HHG also follows ionisation signal and now that ionisation rate is dependent on orientation, experiments studying two-centre interference of HHG from H$_2$ were possible [181] as well as similar experiments on CO$_2$ [182,183]. This approach was later used in the molecular tomography of N$_2$ [184]. Therefore, investigations and application of angle dependent strong field processes can provide insight into the structure of the molecule.

Hydrogen being the simplest molecule can be helpful in validating and improving strong-field theoretical molecular models that can later be applied to more complex
molecules. For example SFA models were modified with respect to the contributions from excited states and ground states using comparisons with TDSE simulations [179]. Similarly the ADK ionisation rates were corrected to include vibrational frequencies in order to predict the orientation dependent ionisation rates for H$_2$ [178]. We believe that an easily measurable parameter like angular offset with benchmarking species like H$_2$ in the experimental labs can add to the available set of valuable data in helping create better theoretical models.

Since the electrons involved in H$_2$ form a sigma bond, it is difficult to polarise H$_2$ as compared to other diatomic molecules, i.e. N$_2$ or O$_2$. Although there were experimental studies in regards to alignment of molecular hydrogen ions [185], only recently (to the best of my knowledge) neutral H$_2$ was aligned [186] by populating specific ro-vibronic levels. However, in the current thesis, we employ ion-electron coincidence measurements of the electron and the proton (H$^+$) resulting from the dissociation of H$_2$ molecule. Since the dissociation occurs along the molecular axis, the direction of proton defines the alignment of the molecule. Hence, we post-select only those protons that are in the desired orientation, requiring no alignment of the molecule initially.

6.3.2 Why attoclock?

Pump-probe experiments have been used widely in order to study molecular dynamics. However, to see electron dynamics that occur at sub-femtosecond timescales or events that require sub-femtosecond accuracy, one need to go shorter than femtosecond pulses. The development of attosecond sources allowed experimentalists to perform XUV-IR pump-probe experiments [187]. In contrast, the technique of AAS offers an accuracy of few attoseconds without requiring attosecond pulses. For a typical central wavelength of 800 nm attoclock offers an accuracy of 1$^\circ$ $\approx$ 7 as. To achieve the same in a pump-probe technique with femtosecond pulses, one needs to at least have a variable delay in steps of 3 as which would correspond to a path difference of 1 nm between the two pulses. Such an accuracy is an impossible task to achieve with preserving the attosecond resolution, as the temporal resolution is limited by the pulse duration. Hence, applying the attoclock technique appropriately could prove to be an alternative tool in understanding molecular (electron) dynamics.
The following section makes such an attempt to create a technique that uses alignment dependent angular offsets of \( \text{H}_2 \) in trying to understand the dynamics. Though the experiment is similar to that of the angular streaking done on atoms that determined tunnelling delays, the analysis performed on the data utilising the SF-MFPMD to calculate offsets is first of its kind in the literature. The experimental studies will be compared to the preliminary theoretical data and the possible implications would be drawn from the available data.

### 6.4 Experimental Data

The experimental set-up and data acquisition are identical to the ones described in Chapter 5. The molecular hydrogen from a pressurised bottle enters the gas beam line through differential stages and skimmers turning it into a supersonic cold gas jet, which interacts with the laser pulse in the REMI. The experiment was performed with both multi-cycle pulses (28 fs) of intensity \( 4.2 \times 10^{14} \text{ W/cm}^2 \) and few-cycle (7 fs) pulses of intensity \( 4.1 \times 10^{14} \text{ W/cm}^2 \) with an ellipticity of 0.84 ± 0.01, as described in the following subsections.

#### 6.4.1 Multi-cycle pulses

Strong-field interaction with \( \text{H}_2 \) can generally lead to bound ionisation \( \text{H}_2^+ + e^- \), dissociation \( \text{H}^+ + \text{H} + e^- \) or double ionisation \( 2\text{H}^+ + 2e^- \). We perform a coincidence measurement between ions and electrons to choose electrons correlated to the ions generated from a specific channel. The supersonic gas jet enters the REMI through an adjustable slit such that the total ionisation events (including all species) \( \ll 1 \) per pulse, ensuring little possibility for false coincidences.

We initially select the desired ionic species based on their mass. By choosing an appropriate window based on the TOF of ions, we can separate bound ionisation \( \text{H}_2^+ \) from the dissociation and double ionised \( \text{H}^+ \), shown in Fig.6.3 in momentum plane. Since bound ionisation leads to a single ion and electron requiring no bond-breaking, this can be considered as a streaking experiment with a complex atom. Hence, we shall expect the electron-ion pair to be streaked and gain momentum by mutually conserving it. This shall result in the final momentum of the ion to be along \( \theta + 90^\circ \).
Determining the peak field

The dissociated or Coulomb exploded H$^+$ are produced through bond breaking and therefore they fly away along the direction of the molecular axis. Although the hydrogen molecules are oriented randomly, the probability of ionisation or dissociation is maximum along the peak field, shown in Fig.6.3(a). Since dissociation occurs slower as compared to the double ionisation event, the effect of streaking on double ionised fragments is the weakest. Hence, we use the peak MD of doubly ionised fragment ions as the indicator for determining the peak field, i.e. the major axis of the polarisation ellipse. This would accomplish the job of polarimetry as the first marker to determine the angular offsets. Since this is done in the frame of REMI, one does not need to calibrate the laboratory axis to REMI’s axis, as done in Sec.5.3.

To achieve this, we use the fact that the kinetic energy of the Coulomb exploded fragments is much higher than the dissociated ones. Therefore an appropriate window of kinetic energy is used to separate these two channels, as shown in Fig.6.4(b).
CHAPTER 6. ATTOCLOCK STUDIES ON DISSOCIATIVE DYNAMICS OF H₂

Figure 6.4: (a) Shows the MD of the dissociated and double ionised fragments. (b) Shows MD of the only the double ionised H⁺ post filtering the lower kinetic energy ions. (c) Shows a double Gaussian fit for the counts integrated radially from the MD of the double ionised H⁺ in the polarisation plane. The peak is found to be at 83.97° ± 0.51°.

We follow identical procedure as done in the case of electron-MD in Sec.5.3, to remove any possible systematic offsets while analysing the data. The peak PMD is then found at 83.97° ± 0.51°, by fitting a double Gaussian function to the radially integrated counts binned in angular bins of 2°, as shown in Fig.6.4(c).

Alignment dependent offsets

Once the major axis of the polarisation ellipse is determined, we would like to determine the alignment dependent offsets. As mentioned earlier, we infer the direction of molecular axis by choosing the dissociated fragments in a specific direction. Ionisation of the H₂ is a precursor for the dissociation process. This precursor is very important while studying the dynamics, as the electron’s initial momentum can be considered to be zero. If chemical bond breaks before ionisation, the electron would be carrying an initial velocity equal to that of the fragmented proton, complicating the modelling and simulations while analysing results. This can be confirmed experimentally by observing the MD of dissociated ions to its corresponding electrons.

The MD of ions in Fig.6.5(a) now represents the molecules in various orientations. We can post-select the events or fragments that are at a specific angle and plot their corresponding electron PMD. We chose orientations in steps of 20° as shown by the white pie chart in Fig.6.5(a). Steps of 20° were chosen as a compromise between the SNR and the number of orientations required to see a qualitative trend clearly.
Figure 6.5: (a) Shows the MD of dissociated H\textsuperscript{+} fragments, by looking only at lower kinetic energy ions. The peak of the MD in this case is approximately along the same direction as with that of the doubly ionised fragments. The faded pie chart in white colour shows the angular bins of 20\degree considered in choosing the molecular orientation. Please see this in relation to Fig.6.6 for better understanding. (b) Shows the electron PMD corresponding to the dissociated fragments (in all orientations), after applying a coincidence filter. The peak PMD is 90\degree + \theta away from the peak PMD of ions and coincides with that of H\textsubscript{2}\textsuperscript{+} in Fig.6.3(b), suggesting that ionisation precedes dissociation.

Figure 6.6: The final momentum of dissociated fragments determine the molecular axis. The dissociated ions at an angle of (a) 0 – 20\degree (b) 80 – 100\degree (c) 180 – 200\degree and (d) 260 – 280\degree are shown in the left side of the panels. The electrons (which are ionised even before dissociation) PMDs corresponding to these orientations are chosen by coincidence measurements on the right side of the panels.
CHAPTER 6. ATTOCLOCK STUDIES ON DISSOCIATIVE DYNAMICS OF H₂

Using the electron PMD for different orientations angular offsets are determined using the procedure detailed in Sec. 5.3. The angular offsets are plotted as a function of orientation as shown in Fig. 6.7. Though the orientation is defined originally in the REMI’s frame, we convert it into the molecular frame relative to the peak field i.e. \( \Theta' = \Theta - \theta_{\text{ellipse}} \) where \( \Theta' \) is the angle in the molecular frame, \( \Theta \) is the orientation angle in REMI’s frame, \( \theta_{\text{ellipse}} \) is the orientation of the polarisation ellipse defined by the major axis. The error bars are determined from the 95% confidence bounds given by the double-Gaussian fitting routine.

Since the molecular ion (\( \text{H}_2^+ \)) during dissociation has no longer has its charge with spherical symmetry like atomic H, it is not necessary to expect a symmetry in the electron PMD. Therefore the angular offsets for each lobe have been calculated and plotted individually as shown in Fig. 6.7. We see an interesting qualitative trend in the angular offsets as a function of molecular orientation from both lobes. On observing a qualitative sinusoidal trend, a Fourier function, given by

\[
\begin{align*}
f(\Theta') &= a_0 + a_1 \cos(w\Theta') + a_2 \sin(w\Theta') \\
\end{align*}
\]

is used to fit the data obtained by averaging the two lobe offsets. We see that a periodicity of \( \sim \pi \) with \( w = 1.96 \). The modulation depth observed is \( \sim 8^\circ \) which is beyond the error bars indicating a real variation as a function of orientation. At every successive angle of molecular orientation at \( (2n + 1)\pi/4 \) (\( n \) being an integer number), we find a maximum change in the relative offsets.

The Fig. 6.7(b) also shows the angular offsets relative to the angular offset calculated from the bound ionisation (stable undissociated \( \text{H}_2^+ \) in \( 1s\sigma_g \) channel. The ionised molecule in its ungerade state (\( 2p\sigma_u \)) is unstable and the intermolecular distance tends to increase with the electron density locally migrating from one proton to the other. In such a context, the process of dissociation is said to end when the electron density gets localised onto one of the protons’ side and this was observed to occur around \( \sim 15 \text{ fs} \) [188]. After the dissociation process ends, the ionised electron experiences the Coulomb force from the dissociated proton, unlike in the case of un-dissociated ion. We believe that this signature of electron localisation is captured in the asymptotic momentum of the electron and thereby in the relative angular offsets of dissociated vs the bound ionisation electrons.
Figure 6.7: (a) Shows an illustration of how the alignment dependent offsets are plotted. The orientation of the molecule is defined in the laser polarisation ellipse’s frame. Due to the usage of multi-cycle pulse, we would observe two lobes in electron PMD, namely lobe 1 and lobe 2 with their angular offsets being $\theta_1^{\text{offset}}$ and $\theta_2^{\text{offset}}$, respectively. (b) Data presented for the offsets observed as a function of molecular orientation in the laser’s reference frame ($\Theta'$). Red stars represent the offsets calculated from lobe 1 and blue circles are offsets for lobe 2. The blue solid curve is a Fourier function fitted to the average offsets calculated from both the lobes. The left Y-axis shows the scale of the conventional angular offsets measured in the laser frame with black dashed line representing zero-reference line. The right Y-axis shows the angular offsets measured relative to that of the bound ionised $H_2^+$ electrons' offset ($\theta_{H_2^+}$) with the red-dashed line showing the zero-reference line.

Although, the angular offset for bound ionisation channel can be determined using $H_2^+$ PMD as shown in Fig.6.3(b), we choose electron PMD due to its better resolution. The bound ionised electrons are selected through post-processing filter that allows electrons and ions measured in coincidence and conserve momentum mutually. Since we have not pre-aligned the molecules, we cannot retrieve alignment dependent information about undissociated molecules. Therefore the angular offset of the bound ionised electron PMD ($\theta_{H_2^+}$) is determined to be $5.56^\circ \pm 0.59^\circ$, similar to the case of atoms. The angular offsets of the bound ionised channel are equal within the errorbar, ensuring that the $H_2^+$ ion acts as one central positive charge. This was subtracted from the alignment dependent offsets and the right Y-axis in red colour shows these offsets in the plot. It is interesting to see that the alignment dependent offsets are modulated about $\theta_{H_2^+}$ almost symmetrically (considering the error bars of $\theta_{H_2^+}$ and $\theta_\text{offset}$).
6.4.2 Few-cycle pulses

While the dissociation occurs in presence of the field in case of multi-cycle pulses (FWHM of 28 fs), we can study the effect of field-free dissociation using few-cycle pulses (FWHM 7 fs). The few-cycle pulse ionises the molecule and induce the dissociation process. But with the pulse being so short, dissociation completes in a field-free environment. Therefore in comparison to the multi-cycle pulse case, the electron here sees a similar interaction from the ion and the flying proton post field-free dissociation, but it interacts with the field for a shorter time.

The alignment dependent offset experiment was carried out at the intensity of $4.1 \times 10^{14} \text{ W/cm}^2$ using an elliptically polarised pulses of ellipticity $0.85 \pm 0.01$. The CEP of the few-cycle pulse was not stabilised, as done in the case of atomic hydrogen experiment. The double-ionisation channel using few-cycle pulses is not as dominant as it was in the case of multi-cycle pulse. Hence, the major axis of the polarisation ellipse is determined using polarimetry as done in the case of atomic H, but using argon (see Fig.6.8(d)). The Fig.6.8(a)-(c) shows the ion and electron MDs for bound ionised $\text{H}_2^+$ ions, its corresponding electrons and dissociated $\text{H}^+$ respectively.

The plot in Fig.6.9 shows the alignment dependent offsets in the laser polarisation ellipse frame. Similar to what was seen with multi-cycle pulses, we see a modulation in the offsets, but with larger error bars. The larger error bars are partly due to
Figure 6.9: A plot for the angular offsets of two lobes (red star for lobe 1 and blue circles for lobe 2) in PMD as a function molecular orientation $\Theta'$.

The left Y axis shows the absolute angular offsets and the right Y axis in red colour shows the angular offsets relative to the PMD corresponding to bound ionisation channel. The blue analytical fit is Fourier function as mentioned in Eqn.(6.1) for the average offsets calculated from both the lobes.

The propagation of errors from the polarimetry measurement which was small when done in the multi-cycle pulse case with double ionised MD. We again use the Fourier fit as in Eqn.(6.1) to fit the average of both the lobes’ offsets. We also scale these offsets (as shown with the right Y axis with red colour) relative to the angular offset determined from the bound ionisation PMD.

In contrast to the multi-cycle case, the average angular offset is found to be $10^\circ$ higher i.e. $\sim 16^\circ$. But the modulation depth is only around 5-6$^\circ$ which is lesser than the former scenario. Also the crest and troughs of the modulation occur around $30^\circ$ unlike the previous case. However, one identical thing to be noted is that the relative offsets with respect to bound ionised PMD ($\theta_{H_2^+}$) are the same. A symmetric modulation is observed around $\theta_{H_2^+}$.

### 6.4.3 Numerical simulations

In order to understand the complex dynamics underlying the alignment dependent offsets, some preliminary numerical results are presented here. The numerical simulations were provided by Dr. Vladislav Serov and Prof. Anatoli Kheifets. As
CHAPTER 6. ATTOCLOCK STUDIES ON DISSOCIATIVE DYNAMICS OF H$_2$

Figure 6.10: (a) Shows the plot of PMD of H$_2^+$ calculated using numerical simulations based on [189,190]. Simulations were done using elliptic polarised light of ellipticity 0.85, intensity 4.2 × 10$^{14}$ W/cm$^2$ with a Gaussian envelope of FWHM 7 fs with CEP offset being 0. (b) Radially integrated counts of PMD plotted as a function of streaking angle in the polarisation plane for parallel (blue line) and perpendicular (red line) orientation of the molecule relative to the peak field. (c) Shows radially integrated counts of PMD for CEP offset 0 (blue dashed line) and π/2 (red thick line) for the same parallel orientation of the molecule.

In this study, the initial numerical results are done to verify if any angular offsets variations could be observed due to the alignment of the molecular ion in its bound state. Hence, the simulations produce photoelectrons corresponding to H$_2^+$, not leading to any further dissociation. A frozen-core Hartree-Fock method was used for the transition to the single-electron approximation (see section III in [189]), giving the TDSE with effective Hamiltonian. Thus electron-electron correlations are not considered dynamically and the internuclear distance between the two protons is constant and equal to the equilibrium distance of 1.4 a.u. The external field is represented in the velocity gauge with an intensity of 4.2 × 10$^{14}$ W/cm$^2$ and an ellipticity of 0.85. The field in its intensity is varied considering a Gaussian envelope with FWHM of 7 fs. TDSE was solved using the discrete variable representation method (DVR) for the space coordinates and split-operator method for the time evolution of the wavefunction. For the extraction of ionization amplitudes from the
The plots of the PMD and the radially integrated counts in the polarisation plane are showed in Fig.6.10. Calculations were done for parallel and perpendicular orientation of the molecule at CEP $0$ and $\pi/2$. It is clear from the results shown in the Table 6.1, that the offsets are independent of CEP within the error bars. However from Fig.6.9, we expect an offset difference of $\sim 5^o$, which is not reproduced by the theory. Given that the model is quite simple and assumes SAE, frozen nuclei model and ionisation with no dissociation process, one needs to further improve the model to reproduce and understand the experimental data.

Table 6.1: Angular offsets from numerical simulations

<table>
<thead>
<tr>
<th></th>
<th>Parallel</th>
<th></th>
<th>Perpendicular</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>lobe 1</td>
<td>lobe 2</td>
<td>lobe 1</td>
</tr>
<tr>
<td>$CEP=0$</td>
<td>$-11.09^o \pm 0.28^o$</td>
<td>$-9.30^o \pm 0.28^o$</td>
<td>$-11.20^o \pm 0.31^o$</td>
</tr>
<tr>
<td>$CEP=\pi/2$</td>
<td>$-10.92^o \pm 0.28^o$</td>
<td>$-9.49^o \pm 0.28^o$</td>
<td>$-11.01^o \pm 0.30^o$</td>
</tr>
</tbody>
</table>

6.4.4 $H_2/D_2$

The contributions to the angular offset i.e. the asymptotic momentum of the ionised electron is influenced by the internuclear dynamics coupled with electron migration before dissociation and the flying proton post dissociation. In order to verify the effect of nuclear mass on angular offsets, an experiment was performed with a 50:50 gas mixture of $H_2$ and its isotope $D_2$. The advantage of performing such an experiment with mixed gas is that the data is acquired simultaneously for both the gases, removing any possible systematic offsets arising from intensity fluctuations or drifts in the laser output. However the laser parameters could not be kept identical to that of the previous runs and therefore the experiment was performed with few-cycle pulses at a somewhat higher intensity of $4.5 \times 10^{14}$ W/cm$^2$ and the multi-cycle experiment was performed at a lower intensity of $3.6 \times 10^{14}$ W/cm$^2$.

Due to the identical mass of the dissociated $D^+$ and $H^+_2$, these ions reach the detector soon one after the other, yet with different kinetic energy. The bond dissociation energy in $D_2$ is carried by the fragments making them appear as the
Figure 6.11: (a) Shows the MD (in log scale) of $H_2^+$ in the centre along with the dissociated fragments of $D^+$ from $D_2$. They appear concentrically in their momentum in the polarisation plane, due to identical mass. These are separated by choosing appropriate window in the kinetic energy of the ions. (b) Shows the plot of the detected ions as a function of their TOF in REMI. The dissociated $D_+$ appear as the sidebands for $H_2^+$ ions due to their identical mass but different kinetic energy.

Sidebands of $H_2^+$ as shown in Fig.6.11(b) and appear around to it in the MD in the polarisation plane (see Fig.6.11(a)). Hence using a proper region of interest based on kinetic energy can easily isolate the two signals from one another.

Figure 6.12: Measurements showing the relative angular offsets (averaging from both the lobes) of $H_2$ with respect to $D_2$ in their dissociation channels. (a) is the plot for multi-cycle pulse and (b) is the few-cycle pulse data.

The relative angular offsets are measured between the PMD of both the isotopes as a function of molecular alignment in the laser frame of reference. Plots for both multicycle and few-cycle pulses are shown in Fig.6.12(a) and (b), respectively. The
relative angular offsets trend looks pretty flat and no difference beyond the error bars is clearly found. Most of the data goes through the zero reference line, except for few outliers. This shows that the modulation we see for hydrogen is also seen for its isotope. This recent H$_2$/D$_2$ results would now be taken into consideration as a feedback in the ongoing project to improve the current theoretical model to model the complex dynamics involved in understanding the alignment dependent offsets.

6.5 Summary

The recent experimental investigations undertaken in applying attoclock to the molecular systems is presented. As part of it we chose the simplest benchmarking molecular system, H$_2$. Unlike atoms, the molecular dynamics is far more complex due to their extra degrees of freedom. With the vast source of experimental evidence already being present for alignment dependent strong-field studies, we performed experiments to understand the alignment dependent studies using attoclock technique. Instead of pre-aligning the molecule and studying it using a conventional pump-probe scheme, we utilised the dissociated fragments to infer the molecular orientation. The PMDs corresponding to various orientations of the molecule are acquired by measuring electrons in coincidence with the dissociated ion fragments of that particular orientation. The experiment was performed with both multi-cycle pulse and few-cycle pulse to study the effect of both field being present and field-free dissociation.

The experimental results showed a sinusoidal-type modulation in the angular offsets about a static value with a periodicity of $\pi$. The static value of offset also coincides very closely with the offset observed with electrons from the un-dissociated bound-state H$_2^+$. While a larger static value was observed for the few-cycle pulse, the modulation depth was larger for the multi-cycle pulse beyond the error bars. Also in all the cases the crests and troughs of the modulations were around $30 - 45^\circ$. Thus from the above information we can interpret that the modulation we see is a pure alignment dependent effect. In an attempt to explain the observed offsets, initial numerical experiments were performed for few-cycle pulses considering the frozen nuclei model with SAE approximation. The theory failed to produce the alignment
dependent offsets suggesting improvements either in examining the electron-electron correlations and nuclear vibrations.

One of the above issues was examined experimentally by performing the experiment with hydrogen and its isotope. Both species showed same behaviour as a function of alignment, resulting in no relative offsets within the error bars. Hence, we conclude that the present experiments are not sensitive enough to measure the effect of inter-nuclear dynamics on the offsets. Having said that, the current analysis is very useful in developing the current theoretical model that can afford to still work in the frozen-nuclei framework but shall include electron-electron correlations. Simultaneously, experimental efforts shall be invested in making the experiments sensitive enough to detect any possible effects inter-nuclear dynamics on the angular offsets.
This chapter provides a brief recap of the chapters presented in the thesis. In addition to the concluding remarks, the chapter also discusses the future directions on both the experimental and theoretical front based on the experiments presented in this thesis.

7.1 Summary of the research

The main results of this thesis are related to the measurements performed using attoclock technique on the simplest atomic system i.e. atomic hydrogen for understanding the tunnelling dynamics. Attoclock is a precision measurement technique based on streaking that utilises a single near-circular (elliptical) polarised few-cycle laser pulses that maps ionisation times to the electron’s asymptotic momentum. The first 3 chapters are dedicated to the introduction and motivation of the thesis’ main results. They introduce, define, discuss and put the tunnelling time problem in context. They finally end by showing why tunnelling time measurements using atomic hydrogen is need of the hour in resolving the ongoing debates.

The importance of atomic hydrogen as benchmarking species in strong-field physics is illustrated via the first experiment carried out by the author. The aim was to measure the absolute CEP offsets in comparison to noble gases Ar, Kr, and Xe at intensities 1.2 × 10^{14} W/cm² and 2.4 × 10^{14} W/cm². The experiments were carried out using the atomic H beamline constructed in conjunction with a home-built flight mass spectrometer. The results of H were well supported by the \textit{ab initio} 3D-TDSE simulations, while a systematic offset of 0.25\pi radians was observed and reported between the numerical simulations based on SAE and the experiments; thus pointing out the failures of widely used strong field models and approximations describing light matter interaction with complex atoms and molecules.
The second set of experimental data presented are the attoclock measurements performed using atomic H and were carried out in a REMI. It was necessary to build the atomic H beamline integrating atomic H source with REMI. Although previous experiments claimed to have measured non-zero tunnelling times, they used complex atoms with no full *ab initio* theories to rightly interpret the results. The experiments were performed within an intensity range of $1.65 \times 10^{14}$ W/cm$^2$ with an ellipticity of 0.84 using 6 fsec pulses. The REMI can help in reconstructing the 3D MD of the electron post ionisation, giving us the required observable i.e. angular offsets to infer tunnelling times. The angular offsets measured followed an expected trend as in the previous experiments. These results were in good agreement with the *ab initio* full solution of 3D-TDSE results, mutually validating the theory and experiments. However, when the same 3D-TDSE numerical codes were run with short range Yukawa potentials, the angular offsets were no more present. These results strongly suggest that the entire angular offsets were purely manifesting due to the Coulomb force exerted by the parent-ion on the outgoing electron. The measurement enabled us to put an upperbound of 2 as on tunnelling times, in contrary to the previous measurements that were an order of magnitude higher.

The final set of experimental data presented are the attoclock measurements performed on a benchmarking molecular system H$_2$. The attoclock experimental data is now analysed in the context of SF-MFPMD. In other words, we measure the angular offsets as a function of the molecular alignment. In contrast to the pump-probe alignment measurements, we chose to post select the electrons in the acquired data in a way that they correspond to the ion fragments dissociated in a specific orientation. Since ionisation is a precursor to the dissociation process, the electron’s most probable initial momentum at the tunnel exit is still zero, just like in the case of atoms. The experiment was performed using multi-cycle pulses (28 fs) and the few-cycle pulses (7 fs). Both the data sets show a sinusoidal kind variation with a periodicity of $\pi$, about a static angular offset value that coincided with the bound molecular ion’s offset. Thus it was concluded that the modulation was purely an alignment dependent effect. Initial numerical simulations were performed to explain the dynamics. The model used for this purpose was to consider bound molecular hydrogen with no nuclear vibration and a SAE interacting with the 0.85 elliptic
polarised 7 fs field of intensity $4.2 \times 10^{14}$ W/cm$^2$. Relative offsets of $< 1^\circ$ were observed when the simulations were performed for the parallel and perpendicular orientations of the molecule relative to the peak field.

Further experimental investigations were undertaken in finding any possible relative offsets that can be detected due to inter-nuclear dynamics. In order to achieve this the experiment was performed using H$_2$/D$_2$ mixed gas. The alignment dependent offsets were both qualitatively and quantitatively same (within the error bars) for these species. Thus we could conclude the present data and the experimental set-up as it existed was not sensitive enough to detect the inter-nuclear dynamics in these molecules. Following these experimental results, it is now possible to model problems that can abandon nuclear motion but consider the electron-electron correlations present in the molecule to understand the dynamics better.

### 7.2 Future directions

One of the near future experimental projects that is to be accomplished in the Australian Attosecond Science Facility (AASF) is the scaling of angular offsets with changing Noble gas species. Although there are some theoretical works regarding this [191], no experimental study exists till date. As first step, one would like to perform experiment simultaneously with H and He. The relative offsets that can be measured between the simplest atomic system and the simplest system involving multi-electron dynamics, would add to the valuable data based on which the strong-field models relying on SAE can be validated and further improved.

The second most important project would be to transfer the technique of attoclock to complex molecules. Currently, the theory groups are investing their efforts in understanding the SF-MFPMD offsets in hydrogen. Results of these experiments would prove extremely beneficial in modelling molecular dynamics at the simplest level. The attoclock experiment with atomic hydrogen has established that the offsets carry the signature of the Coulomb force from the parent ion. Therefore it is straightforward for the trajectory of the electron to differ with the molecular orientation, due to its asymmetric charge distribution. The field directs the tunnelled electron along a fixed direction, given by the peak field, while molecule is rotated.
Hence, the angular offsets could possibly carry the footprints of the molecular orbital as we scan through different orientations. This could potentially be useful for applications like tomography, determining electron localisation and the dissociation dynamics with few attoseconds precision requiring no pump-probe scheme.
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Appendix A

List of publications and personal contributions

All of the publications listed here are obtained during my PhD candidature (in a chronological order). My contributions are mentioned below. The published articles can be found in the Appendix B.


- I assisted in setting up the experiment, data collection and manuscript preparation.


- I assisted in setting up the experiment, data collection and manuscript preparation. This publication forms the later part of Chapter 1 in the thesis.


143

- Lead experimentalist. I integrated the atomic hydrogen source to the REMI, set-up the experiment, conducted data collection with the REMI and post-processed data using Cobold-PC, Matlab and Mathematica. I prepared the manuscript and this forms Chapter 5 of the thesis.


- I assisted in setting up the experiment, data collection and manuscript preparation.


Relativistic non-dipole effects in strong-field atomic ionization at moderate intensities. arXiv preprint arXiv:1808.00137. Currently, the manuscript is under review.

- I assisted in setting up the experiment, data collection and manuscript preparation.


Attoclock and quest for tunnelling time in strong-field physics (tentative title) Invited article for a special edition: Manuscript under preparation. This forms Chapter 2,3 and 5 in the thesis.

- Literature review and manuscript preparation (based on the current thesis).
Appendix B

Published articles
Precise and Accurate Measurements of Strong-Field Photoionization and a Transferable Laser Intensity Calibration Standard

W. C. Wallace,1,2 O. Ghafur,1,2 C. Khurmi,1,2 Satya Sainadh U,1,2 J. E. Calvert,1,2 D. E. Laban,1,2 M. G. Pullen,1,2,* K. Bartschat,1,2,3 A. N. Grum-Grzhimailo,4 D. Wells,5 H. M. Quiney,5 X. M. Tong,6 I. V. Litvinyuk,2 R. T. Sang,1,2 and D. Kielpinski1,2,

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Ionization of atoms and molecules in strong laser fields is a fundamental process in many fields of research, especially in the emerging field of attosecond science. So far, demonstrably accurate data have only been acquired for atomic hydrogen (H), a species that is accessible to few investigators. Here, we present measurements of the ionization yield for argon, krypton, and xenon with percent-level accuracy, calibrated using H, in a laser regime widely used in attosecond science. We derive a transferable calibration standard for laser peak intensity, accurate to 1.3%, that is based on a simple reference curve. In addition, our measurements provide a much needed benchmark for testing models of ionization in noble-gas atoms, such as the widely employed single-active electron approximation.

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Ionization by strong laser fields drives processes ranging from attosecond pulse generation [1,2] to filamentation [3] and remote lasing [4]. Measurements of strong-field ionization have revealed complex and surprising qualitative features [5,6] that can depend sensitively on the laser intensity. Precise measurements of strong-field ionization are now being used to probe fundamental physics, such as time delays in photoionization [7], but there is substantial evidence that small systematic offsets in these measurements can obscure the results [8]. In frequency metrology, measurements of atomic transitions are affected by systematic errors arising from the ac-Stark shift and laser intensity uncertainty, thereby limiting the precision of the result [9]. Accurate reference data on strong-field photoionization and laser intensity, especially in the attosecond science regime, are therefore needed for further progress on these questions.

In recent years, our group has used atomic hydrogen (H) to perform quantitatively accurate strong-field measurements that are demonstrably free from systematic errors [10–12]. These measurements are performed in the regime of laser pulse durations and peak intensities that are most widely used in attosecond science. As the simplest electronic system, H has long been recognized as a benchmark species for strong-field physics experiments [13,14]. Direct integration of the three-dimensional time-dependent Schrödinger equation (3D TDSE) enables high-accuracy simulation of H and less than 1% error, with only very minor approximations [15]. Hence, the accuracy of the H data can be certified by their agreement with 3D TDSE simulations.

Here, we use these techniques to perform accurate measurements of the strong-field ionization yield from three commonly used noble-gas targets, and to derive a transferable, high-accuracy calibration standard for laser intensity. Our data enable accurate intercomparisons of data taken at various strong-field laboratories, and improved simulations of complex phenomena involving strong-field ionization, such as filamentation, high-harmonic generation, and laser-induced electron diffraction. We use the noble-gas data to derive a calibration standard for laser peak intensity, given by a simple reference curve, that offers an order of magnitude better accuracy than previous transferable standards [16,17]. Our intensity calibration standard applies to an intensity regime that is readily transferable to laboratories using few-cycle 800 nm laser systems, including most attosecond science laboratories.

The experimental apparatus is detailed in Refs. [10,11]. It consists of a well-collimated atomic H beam skimmed from the output of a rf discharge dissociator, which intersects the focus of an intense few-cycle laser. The flux of our custom-constructed atomic source is several orders of magnitude higher than commercial sources [18], facilitating a high signal level. The laser generates pulses with rapidly varying carrier-envelope phase of 5.5 fs duration (measured at full-width at half maximum of intensity) with a central wavelength of...
800 nm. Pre- and postpulse effects were observed to be minimal due to the absence of sidelobes in the autocorrelation trace. Ions are created in the overlap region between the atomic beam and the laser beam, and are detected with an ion time-of-flight (ion TOF) mass spectrometer. A microchannel plate located at the end of the ion TOF detects the ions and outputs a voltage proportional to the ion yield (see Supplemental Material [19]). The overlap region is well defined, allowing us to account accurately for focal-volume averaging (FVA) effects [12].

The measured yield of H\(^+\) ions resulting from ionization of atomic H over a range of laser peak intensities is shown in Fig. 1. This yield, denoted \(Y_{H^+}\), is accurately measured by removing contributions arising from ionization of undissociated H\(_2\) in the beam, and background H\(_2\)O vapor. These contaminant signals can be as large as 9.5% of the desired \(Y_{H^+}\), and hence must be removed to obtain percent-level accuracy. Errors in \(Y_{H^+}\) accumulate from microchannel plate voltage baseline subtraction, from short- and long-term laser drifts, and from uncertainties in determining the dissociation fraction. A detailed account of the analysis and error estimation is given in the Supplemental Material [19].

We certify the accuracy of our data by comparison with accurate 3D TDSE calculations. As in our previous work [10,11], we perform FVA over the interaction volume, assuming a Gaussian laser profile and a molecular beam of diameter \(d\), where \(d\) is much smaller than the laser Rayleigh range and much larger than the transverse size of the laser beam. Under these conditions, the FVA becomes independent of beam propagation effects [12]. Effects of carrier-envelope phase on the theoretical yields were negligible. We perform a weighted least-squares fit of the 3D TDSE yield predictions to the \(Y_{H^+}\) data using a function of the form

\[
P_{H^+}(I_{\text{est}}, A, \eta_1) = AS(\eta_1 I_{\text{est}}).
\]

Here, \(A\) and \(\eta_1\) are the fit parameters, while \(S\) is the focal-volume averaged and carrier-envelope-phase averaged theory model evaluated at the actual laser intensity \(I_0 = \eta_1 I_{\text{est}}\). The independently estimated intensity \(I_{\text{est}}\) is obtained from measurements of the laser parameters—waist size \(w_0\), average power \(P\), pulse duration \(\tau_p\), and repetition rate \(f_{\text{rep}}\)—via

\[
I_{\text{est}} = \frac{2P}{\pi w_0^2 f_{\text{rep}} \tau_p}.
\]

The \(\eta_1\) fit parameter is a rescaling coefficient of the laser intensity that accounts for the error in \(I_{\text{est}}\) (often as large as 50%), and permits the accurate retrieval of \(I_0\). The \(A\) fit parameter rescales the yield to account for both the unknown atomic density and detector efficiency, but is irrelevant for intensity calibration.

Figure 1 illustrates the agreement between the \(Y_{H^+}\) data and the 3D TDSE simulations, certifying that our data are free of systematic error to within our 2% measurement precision. A value of \(\eta_1 = 0.641 \pm 0.007\) is found, indicating that we can calibrate the laser peak intensity to a theory-certified accuracy of better than 1.1% without systematic error. Normalized residuals from the fit are shown as percentage deviations from the 3D TDSE predictions in Fig. 1. Neglecting background subtraction shifts \(\eta_1\) by 3.1%, more than our 1.1% accuracy.

Our data are easily able to discriminate between the 3D TDSE and other commonly used theoretical approximations. A well-known alternative to solving the TDSE is the analytic theory of Ammosov, Delone, and Krainov (ADK) [20]. Standard ADK theory is intuitive and straightforward to calculate, but it is known to fail at intensities near to or exceeding the onset of barrier-suppressed ionization [21]. An empirical correction [22] has since been developed to extend the validity of ADK rates to higher intensities. Standard ADK and empirically corrected ADK rates, as well as percentage residuals, have also been plotted in Fig. 1 using the \(A\) and \(\eta_1\) fit parameters obtained from the 5.5 fs 3D TDSE fit. Standard ADK deviates from the data at

---

**FIG. 1.** (a) Experimental data for H\(^+\) yield (solid circles) compared with theoretical predictions from 3D TDSE (dot-dashed line), standard ADK (dashed line), and empirically corrected ADK (Emp-ADK) (dotted line) models. In some cases, the error bars on the data are smaller than the symbols; see Supplemental Material [19] for error estimates. (b) Percentage difference of experimental H\(^+\) yield data and both ADK theories from the 3D TDSE simulations.
high intensities by almost a factor of 2, whereas empirically corrected ADK is accurate at the 10% level there. Nevertheless, the latter model is still clearly ruled out by the data at lower intensities.

We now present demonstrably accurate measurements of the photoionization yield of singly charged argon, krypton, and xenon, providing reference data in a regime for which accurate simulations are not available. Depletion of the noble-gas atoms to multiply charged states was observed but the effect found to be negligible in this intensity regime. The results for the yield of each gas target, denoted $Y_{\text{Ar}}^+$, $Y_{\text{Kr}}^+$, and $Y_{\text{Xe}}^+$, are shown in Fig. 2. The agreement between theory and experiment for H certifies the accuracy of the noble-gas yields, as these measurements were performed in the same apparatus, using identical laser parameters.

Theoretical ionization probabilities for the noble-gas atoms are obtained by solving the 3D TDSE under the single-active electron approximation with the second-order-split operator method in the energy representation [23,24]. The model potentials [22] are calculated by using the density functional theory with self-interaction correction [25], from which the calculated atomic ionization potentials are in good agreement with the measured ones. The theoretical simulations are subjected to FVA for comparison with experimental data. As with the atomic H data, we also compare standard ADK and empirically corrected ADK rates with the noble-gas data, using a weighted sum of $m_l = 0, 1$ for the $p$-orbital ($l = 0$) and ground-state ionization potentials. As a nonrelativistic model was used, the fine-structure splitting was ignored. We note the existence of fast dynamics due to spin-orbit coupling as investigated in [26]; however, analysis of these dynamics is outside the scope of this Letter.

Each of the theory models is compared to $Y_{\text{NG}}^+$ (where the subscript NG denotes one of the noble gases) using the calibrated intensity $I_0$ and the fitting method Eq. (1). The fits and residuals for each target are shown in Fig. 2. Since the intensity is already calibrated by the $Y_{\text{H}}^+$ data, the calibration factor $\eta_1$ is fixed to a value of 1, while $A$ is allowed to vary in order to account for the unknown gas density. While the data are accurate at the 2% level, the theoretical predictions agree with the data only at the tens of percent level, with both ADK rates performing poorly. These data therefore pose a direct challenge to current models which are widely used to predict results from strong-field ionization experiments. Because of the constrained fit parameter, ADK and empirical ADK (Emp-ADK) fits are weighted more heavily towards the higher intensities because the signal-to-noise ratio is higher and the uncertainty is correspondingly lower. This results in an artifact where ADK appears to fit better than Emp-ADK. Removing the constraint on the $\eta$ parameter vastly improves the fit; however, the retrieved $\eta$ is significantly different in comparison to the phenomenological model. While all three theories disagree with the experimental data, Fig. 2 shows that we can achieve good agreement with the data using the following phenomenological model:

![Figure 2](image-url)
PRL 117, 053001 (2016) PHYSICAL REVIEW LETTERS week ending 29 JULY 2016

\[ P_{NG}^{(2D)}(I_{\text{est}}; A, \eta_2) = AS_{\text{phenom}}(\eta_2 I_{\text{est}}), \]  

where

\[ S_{\text{phenom}}(\eta_2 I_{\text{est}}) = \exp[-\alpha(\eta_2 I_{\text{est}}/I_c)^{-1/2}/C_{138} + (\eta_2 I_{\text{est}}/I_c)^\gamma]. \]  

Here, \( A \) and \( \eta_2 \) are the same fit parameters as described in Eq. (1). The coefficients \( \alpha \) and \( \gamma \) are set by fitting Eq. (4) to the 3D TDSE for each gas target. The value of \( I_c \) was determined from the data of Fig. 2 by fixing \( \eta_2 \) to a value of 1, and substituting \( I_{\text{est}} \) with our \( I_0 \) values obtained from the \( H^+ \) fit. The values of these parameters are shown in Table I for each gas target. Our values for \( I_c \) include the uncertainty in the \( H^+ \) calibration as well as the fit error, and demonstrate our ability to calibrate the intensity at the 1.3%, 1.5%, and 2.5% levels using \( \text{Ar}^+, \text{Kr}^+, \) and \( \text{Xe}^+ \) as gas targets, respectively [27]. The value of \( I_c \) is insensitive against the removal of any individual data point from the fit data set, indicating that the model robustly represents the data over the entire intensity range. However, it is important to note that the phenomenological model is introduced purely as a convenience, so that the reader can easily carry out intensity calibration with a closed-form analytic fit function. We emphasize that Eq. (4) is not associated with any model of the ionization physics. Hence, we do not expect it to be valid outside the range of intensities studied here.

Equation (4) enables absolute intensity calibration at the 1.3% level for few-cycle 800 nm laser systems, like those widely used for attosecond science. The calibration only requires a mass spectrometer, a few-cycle laser at 800 nm, and a source of either \( \text{Ar}^+, \text{Kr}^+, \) or \( \text{Xe}^+ \). The intensity range covered by our calibration, \((1-5) \times 10^{14} \text{ W/cm}^2\), is used by most atomic and molecular strong-field physics experiments, particularly attosecond science experiments. Instructions for using our calibration are detailed in the Supplemental Material [19].

Our transferable calibration standard can be shown to reliably determine the absolute intensity without systematic errors; in other words, the retrieved intensity can be accurately expressed in the SI unit of \( W/\text{m}^2 \). Previously presented transferable intensity calibration methods [17,29,30] relied on theoretical approximations whose systematic errors were not fully quantified. The removal of systematic errors, i.e., offsets between the measured value and the “true value” of the measured quantity [28], is crucial for accurate measurement. Therefore, while these previous methods provide relative calibrations of the intensities in the interaction region, their relationship to the SI system of units remains unclear.

Our calibration is relatively insensitive to laser parameters other than peak intensity. As shown in our previous work [11], variations of the pulse duration by 10% may cause a rescaling of the overall yield, but cause < 1% shifts in the retrieved intensity. Similarly, the calibration is not overly sensitive to the precise form of the beam profile: we achieve good theory-experiment agreement for \( H \) with beam \( M^2 \) factors as high as 1.5. In most experiments with molecular beams, including ours, the focal volume averaging is independent of \( M^2 \) so long as the transverse intensity distribution is Gaussian and is constant within the interaction region. As long as these conditions are satisfied, Eq. (4) is expected to hold even for much larger values of \( M^2 \). While the calibration can presently only be used for wavelengths near 800 nm, our simulations show that changes of the wavelength by 50 nm affect the retrieved intensity by < 1%. This lack of sensitivity is expected since our laser bandwidth is > 200 nm. Finally, the calibration can tolerate laser pulse energy fluctuations of at least 0.7% (root mean square), as independently measured on a photodiode. We achieve good theory-experiment agreement for \( H \) at this level. Other laboratories can transfer our calibration standard to lasers of widely different pulse durations or wavelengths, without the use of an \( H \) source, by the following procedure. (i) Calibrate the intensity of a standard few-cycle laser near 800 nm by measuring one of \( \text{Ar}^+, \text{Kr}^+, \) or \( \text{Xe}^+ \) photoion yields. (ii) Measure the ratios of the beam parameters used in Eq. (2) between the new and standard laser. These ratios can be measured much more accurately than the parameters themselves. From these ratios, derive an absolute calibration of the new laser’s intensity. (iii) Measure \( \text{Ar}^+, \text{Kr}^+, \) or \( \text{Xe}^+ \) photon yield as a function of the new laser’s intensity. The data for the new laser are known to be accurate, since they are referenced to our data by steps (i) and (ii). Finally, (iv) construct a phenomenological fitting function for the new data, to be used in the same way as Eq. (3). The Supplemental Material [19] details a method for intensity calibration using apparatus other than an atomic beam.

We have presented photoionization yield measurements with an accuracy that improves on previous measurements by an order of magnitude. Our data are obtained in a regime of laser pulse duration and intensity that is widely used for attosecond science, and can be used to benchmark measurement techniques in that field. The measurements are certified at the percent level through the observation of theory-experiment agreement for \( H \). Using the noble-gas data presented here, other laboratories can verify the accuracy of their measurements, calibrate their apparatus, and obtain similarly accurate data for other atomic and

<table>
<thead>
<tr>
<th>Fit parameter</th>
<th>( \text{Ar}^+ )</th>
<th>( \text{Kr}^+ )</th>
<th>( \text{Xe}^+ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha ) (arb. units)</td>
<td>2.84</td>
<td>4.24</td>
<td>3.71</td>
</tr>
<tr>
<td>( \gamma ) (arb. units)</td>
<td>-3.03</td>
<td>-2.49</td>
<td>-2.69</td>
</tr>
<tr>
<td>( I_c \times 10^{14} \text{ W/cm}^2 )</td>
<td>3.86 ± 0.05</td>
<td>2.06 ± 0.03</td>
<td>1.18 ± 0.03</td>
</tr>
</tbody>
</table>
molecular species. In the meantime, our data provide accurate reference for simulations of strong-field phenomena involving few-cycle ionization. Finally, we have presented a transferable calibration of laser intensity that provides an order-of-magnitude accuracy improvement. The standard is readily accessible to laboratories using few-cycle 800 nm lasers and can be further transferred to other laser systems, enabling the correct measurement and interpretation of intensity-sensitive phenomena in strong-field ionization.

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APPENDIX B. PUBLISHED ARTICLES

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[19] See Supplemental Material at http://link.aps.org/ supplemental/10.1103/PhysRevLett.117.053001 for the methods used for acquisition and analysis of the data that are presented in this Letter, alongside detailed instructions on how to calibrate the laser peak intensity according to Eq. (3) of this Letter.
[27] Per the recommendations of the Joint Committee for Guides in Metrology [28], we have here stated the σ standard deviation for I, i.e., the 68% confidence interval. Therefore, on any particular reproduction of our experiment, the retrieved intensity has a 32% probability of falling outside the 68% confidence interval for purely statistical reasons.
Measuring laser carrier-envelope-phase effects in the noble gases with an atomic hydrogen calibration standard

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We present accurate measurements of carrier-envelope-phase effects on ionization of the noble gases with few-cycle laser pulses. The experimental apparatus is calibrated by using atomic hydrogen data to remove any systematic offsets and thereby obtain accurate CEP data on other generally used noble gases such as Ar, Kr, and Xe. Experimental results for H are well supported by exact time-dependent Schrödinger equation theoretical simulations; however, significant differences are observed in the case of the noble gases.

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Frontiers for few-cycle laser pulses are expanding every day with the generation of short extreme-ultraviolet laser pulses from solid-state targets [1] and production of few-cycle laser pulses in the midinfrared domain [2]. Along with innovative ways to generate carrier-envelope-phase (CEP) stable few-cycle laser pulses with femtosecond repetition rate [3], new techniques are continually explored to accurately measure the laser CEP [4–7].

\[
\vec{E}(t) = |\vec{E}(t)| \cos(\omega_0 t + \phi_{\text{CEP}}).
\]

The electric field of a laser pulse can be described as shown in Eq. (1), where \(|\vec{E}(t)|\) is the pulse envelope, \(\omega_0\) is the carrier frequency, and \(\phi_{\text{CEP}}\) is the CEP of the laser pulse. The CEP specifies the offset between the peak of the pulse envelope and the nearest maximum of the electric field oscillation. An important aspect of the few-cycle laser pulse (\(\lambda_{\text{central}} \approx 780\) nm, one optical cycle \(\approx 2.6\) fs) is that the CEP also affects the processes initiated by the laser pulse when interacting with the matter. The ability to precisely measure the CEP of few-cycle laser pulses is very important for diverse scientific applications such as high-harmonics generation [8, 9], above-threshold ionization (ATI) [10], attosecond pulse generation [11–13], coherent control of molecular dynamics [14–17], and attosecond ionization under the influence of strong laser fields [18, 19].

Generally, photoionization at different laser peak intensities can be described in two broad domains, (i) the multiphoton ionization domain, where simultaneous absorption of multiple photons results in ejection of an electron from the atomic core causing ionization, and (ii) the photoionization tunneling regime, where the potential barrier of the atom is lowered by the intense laser electric field and the electron tunnels through the Coulomb potential barrier. The emitted electron in the latter case can escape the atomic core potential and hit the detector or it may recombine with the parent ion to give rise to high-harmonics generation [20, 21]. The physics behind these processes seems simple but accurately predicting the atomic Coulomb potential and its effects on the electron wave packet is a major challenge for even the most advanced theoretical methods. Recent efforts by Torlina et al. [22] to measure the electron tunneling time also imply the breakdown of key theoretical assumptions in interpreting attoclock measurements for multielectron atoms that are mainly attributed to the delays associated with multielectron dynamics. The work presented in this paper provides accurate and extremely reliable experimental evidence to further the debate in this regard and raise questions regarding the validity of advanced theoretical methods to measure the laser CEP using multielectron atomic species such as Ar, Kr, and Xe.

Experiments by Paulus and co-workers [23] have shown that the CEP of few-cycle laser pulses can be tagged by using Xe atoms as target species. But questions remain about systematic CEP phase offsets in such measurements, since the accuracy of the available theoretical models is not well characterized [24]. However, in the case of atomic hydrogen exposed to an intense few-cycle laser pulse, the time-dependent Schrödinger equation (TDSE) can be solved numerically with high precision and provides a very reliable calibration standard [25–28]. Here, we present the experimental evidence for the measurement of CEP of few-cycle laser pulses in the noble gases by using atomic hydrogen as the calibration standard. In the case of H, we find that the experimental results are well supported by ab initio theoretical simulations; however, for multielectron species such as Ar, Kr, and Xe, the single-active electron (SAE) approximation [29] differs significantly from experimental results.

Figure 1 shows a schematic of the experiment. A commercial Femtosecond Compact Pro laser system with CEP stability is used to generate \(\approx 6\)-fs laser pulses with 780-nm central wavelength at 1-kHz repetition rate. An additional 2-2 fs interferometer (from Menlo Systems) is used to establish CEP feedback and locking near the experimental end station to control slow CEP drifts. A set of matched fused silica wedges (from MolTech GmbH Berlin, 1-mm lateral translation \(\approx 1.25\) rad rad phase shift) is used to vary the CEP of the laser pulses.
The experimental setup to create an atomic H beam has been described in detail elsewhere [30]. The atomic H beam is accompanied by residual H$_2$ and background contributions in the interaction chamber (see the Supplemental Material for more details [31]). At each intensity, three separate laser CEP resolved measurements are taken to isolate atomic H photoelectron yield, namely, with the atomic H source ON (H + H$_2$ + background), atomic H source OFF (H$_2$ + background), and only background. In the case of noble gases, two separate laser CEP resolved measurements are taken, with noble gas source ON (noble gas + background) and background only. All these measurements are performed at the same phase points by repeating the wedge scan with $f$ to $2f$ phase lock; therefore all systematic errors because of H$_2$ and background contributions are canceled out. The systematic errors resulting from change of dissociation fraction ($\pm$5%) of H$_2$ to atomic H contribute $\sim$2% error to the final atomic H photoelectron yield (see the Supplemental Material for more details [31]).

The laser beam is focused into the interaction chamber by using an off-axis parabolic (OAP, focal length = 750 mm, spot size = 45 $\mu$m, Rayleigh length $\sim$10 cm) mirror; it interacts with the atomic H beam in the interaction chamber (polarization = perpendicular to gas flow and along the time-of-flight axis of the spectrometer, atomic beam diameter $\sim$0.5 mm). The peak intensity of the laser pulses was estimated to measure focal spot size, pulse width, and average laser energy. Electrons generated from this interaction are detected by an electron-time-of-flight detection system (EToF). Electrons emitted in only one direction are collected. The EToF spectrometer [Fig. 1(b)] is enclosed in $\mu$-metal to provide shielding from stray magnetic fields. Electrons with different kinetic energies are generated from laser and atom interaction and travel in a field-free region to a microchannel plate. Each electron gives rise to a temporally resolved voltage peak which is recorded using an analog-to-digital conversion card (Agilent, model no. U1084A). Figure 2 shows the CEP averaged electron energy spectra of different atomic species at two laser peak intensities, namely, at 1.2 $\times$ 10$^{14}$ W/cm$^2$ and 2.5 $\times$ 10$^{14}$ W/cm$^2$ (ponderomotive energy $U_p = 7$ and 15 eV, respectively). Solid vertical lines in Fig. 2 represent the 2$U_p$ point which marks the onset of the rescattering domain, where the emitted electron gains enough quiver energy from the laser field to either rescatter from the parent ion or cause further ionization. The electron energy spectra for each atomic species have been offset for the sake of clarity. For CEP resolved experiments, a motorized fused silica wedge is used to vary the laser CEP over a range exceeding 2$\pi$ rad.

The electron energy spectrum is collected at each wedge position (integration time 90 s) representing a laser CEP point. The CEP-dependent electron spectrum is denoted $Y(E,\phi)$, where $E$ is the electron kinetic energy and $\phi$ is the laser CEP. As seen from Fig. 2, $Y(E,\phi)$, which is the laser CEP averaged electron energy spectrum, varies over a wide range so we parametrize the laser CEP effects by the normalized quantity $S(E,\phi)$ that measures the CEP effect at $E$ relative to the CEP averaged electron yield at $E$.

$$S(E,\phi) = \frac{Y(E,\phi) - Y(E,\bar{\phi})}{Y(E,\bar{\phi})},$$

We obtain theoretical simulations for H from numerical integration of the three-dimensional TDSE. These simulations are extremely reliable as demonstrated by our previous work [28]. For multielectron systems such as Ar, Kr, and Xe, the theoretical simulations are based on SAE approximation. The ATI spectra of the rare gas atoms are calculated by solving the TDSE with the generalized spectrum in the energy representation [29,32] under the single-active electron approximation. We use the model potentials [33] obtained by density functional theory with the self-interaction correction [34], which gives the atomic ionization potentials. Focal volume averaging is performed on all simulations for comparison with experimental data.

Figures 3 and 4 show the CEP calibrated experimental data and theoretical simulations for H, Ar, Kr, and Xe. For ease of viewing, both data and theory are smoothed with respect

FIG. 1. (a) Experimental setup for CEP resolved experiments. M1–M3: Reflective mirrors; PNDF: pellicle neutral density filters; OAP: off-axis parabolic mirror; W: fused silica wedge; TMP: turbomolecular pump. (b) Electron-time-of-flight spectrometer. Atomic beam (gray, long dash), laser beam (black, short dash), and laser polarization (red, solid line) directions are shown on bottom left of (b) in a laboratory frame.

FIG. 2. (a) CEP averaged electron energy spectra of different atomic species, namely, Ar (red, dash), H (black, solid), Kr (blue, dotted), and Xe (orange, dot-dash) at two different intensities. (a) 1.2 $\times$ 10$^{14}$ W/cm$^2$($U_p = 7$ eV) and (b) 2.5 $\times$ 10$^{14}$ W/cm$^2$($U_p = 15$ eV). Electron energy spectra for different atomic species are offset for the sake of clarity. Solid vertical lines represent 2$U_p$ point. The $y$ axis has arbitrary units with a log$_{10}$ scale.
to energy using a Gaussian filter with a full width at half maximum (FWHM) of 1.5 eV and the results over the CEP range $0 < \phi < 2\pi$ are replicated over the range $2\pi < \phi < 4\pi$. The Gaussian filter with 1.5 eV FWHM was chosen based on the energy resolution of the EToF detector. Depending upon the ponderomotive energy ($U_p$) of the photoelectron, the results shown in Figs. 3 and 4 can be separated into two domains, namely, above and below $2U_p$, as the photoelectrons in these domains come from two different mechanisms. Below $2U_p$, the photoelectron can come from the tunneling mechanisms caused by one of the several laser electric field peaks (i.e., tunneling occurs over a varied range of phases of the fundamental pulse) and from the subsequent rescattering process from the parent ion. The laser CEP dependence in this regime also depends on the energy of the photoelectron and therefore makes the calibration of laser CEP more complicated [35]. However, the photoelectrons above $2U_p$ originate from a different mechanism. Above $2U_p$, the photoelectrons come from back rescattering from the parent ion. The energy of the photoelectron depends on the largest peak in the laser electric field and the yield of these photoelectrons depends on the peak field strength before the largest one [29]. In this domain, the dependence of laser CEP on the energy and yield of the photoelectron is more stable and we use this domain to calibrate the laser CEP.

It is evident from Figs. 3 and 4 that in the case of H for $\geq 2U_p$, we observe good agreement between experimental data (top panel) and TDSE simulations (bottom panel). It demonstrates that the experimental results are reliable. The experimental data for the noble gases are taken under identical conditions in the same apparatus, so they are expected to be similarly reliable. We can therefore assign an absolute CEP to the data on the noble gases free of systematic errors. For further qualitative analysis, a line-out comparison [Figs. 5(a)–5(h)] is shown between experimental (dotted line, black) data and theoretical simulations (solid line, red) for photoelectron energy of $\geq 2U_p$ for both intensity regimes (see the Supplemental Material for full comparison [31]). For the higher-intensity regime (Fig. 5, right column), in the case of H [Fig. 5(b)], the experimental data and TDSE simulations show good overlap, but the qualitative trends for Ar, Kr, and Xe [Figs. 5(d), 5(f), and 5(h)] show $>0.25\pi$ rad phase offset between experiment and SAE simulations. For the lower-intensity regime (Fig. 5, left column), in the case of H [Fig. 5(a)], there is good agreement between experiment...
An accurate interpretation of the physical phenomenon responsible for these complex CEP resolved photoelectron energy spectra is not trivial. Any such attempts to assign a particular mechanism responsible for observed spectra would heavily depend on the key theoretical assumptions in estimating atomic Coulomb potential, electron rearrangement dynamics after light absorption, and the effect of long-range Coulomb potential on the electron wave packet before it hits the detector. Recent experiments [36] on He atoms using few-cycle laser pulses also suggest that at higher intensities (2–4 × 10¹⁴ W/cm²) the electron correlation effects of bound-state electrons play a significant role in determining the time resolved absorption spectra of autoionizing states. In this paper, the extremely reliable and accurate measurements of the phase offset in H-referenced noble gases are used to expose the weakness of theoretical models based on SAE approximations. These experimental results clearly demonstrate that it is not possible to rely on approximate theoretical methods such as SAE to accurately calibrate the CEP of the few-cycle laser pulses using noble gases. The results from this work can be used to guide and validate all future multielectron theoretical simulations to accurately measure the laser CEP.

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FIG. 6. Experimental phase offset (bin width = 5 eV) for different atomic species at (a) 1.2 × 10¹⁴ W/cm² and (b) 2.5 × 10¹⁴ W/cm². Difference between phase offset from experiment and theoretical simulations for (c) 1.2 × 10¹⁴ W/cm² and (d) 2.5 × 10¹⁴ W/cm². Lines are a guide to the eye. Note that the y axes in this figure are in units of radians.


[31] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevA.96.013404 for isolation of atomic hydrogen signal, systematic H2 error estimation and Fig. 5 with full energy scale.


Ellipticity-dependent fragmentation of acetylene dications

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When an intense laser field interacts with molecules, a variety of characteristic dynamics come into play such as ionization, dissociation, fragmentation, and isomerization. Here we experimentally investigate the effect of laser intensity and polarization of ultrashort laser pulses on dissociative double ionization of acetylene, in particular on the ultrafast proton migration. A significant increase of the relative yield of the proton migration channel versus the symmetric break-up channel with increase in intensity and the change of polarization from linear to circular is observed.

I. INTRODUCTION

In polyatomic molecules, fragmentation reactions are major building blocks of chemistry. Studying how these reactions are affected by parameters of an external electric field is important for understanding their pathways and dynamics and ultimately for the ability to control those dynamics and outcomes. It takes typically from several femtoseconds to picoseconds of time for the nuclear motion that is involved in the breaking of a chemical bond. After removal of electrons, charge density within the molecule redistributes very quickly and the molecule itself undergoes a severe structural deformation. One of the most interesting restructuring processes in hydrocarbons is the proton migration. Proton migration induced by ultrafast laser pulses has become one of the most attractive research topics because it plays an important role not only in restructuring the molecule but also in determining the outcome of the consequent fragmentation process. It is therefore very interesting to learn how this proton migration is affected by various laser parameters and this question has been investigated for various molecules with different laser parameters [1–3]. Breaking of the molecular bonds can be steered into the desired direction by tuning the carrier-envelope phase (CEP) of the few-cycle pulses or by using the phase controlled parallel or orthogonally polarized two-color laser fields [4–6]. The influence of the laser pulse parameters was demonstrated experimentally in the complex fragmentation reaction of ethylene C₂H₄ [7], in particular the effect of laser pulse duration on breaking of chemical bonds. It has been found that parameters of ultrashort laser pulses such as intensity, pulse duration, polarization, and wavelength influence photoinduced chemical processes very strongly.

In the present study, we examine the effect of intensity and polarization on two-body fragmentation channels of acetylene dications, by using the coincidence momentum imaging method.

II. EXPERIMENTAL SETUP

Few-cycle laser pulses with sub-6 fs pulse duration from a Ti:sapphire laser system FEMTOPOWER Compact Pro (Femtolaser) are obtained at the repetition rate of 1 kHz with 750 nm central wavelength, spectrally broadened and then compressed by a neon-filled hollow-core fiber and a chirped mirror compensation. The measurements were conducted in a reaction microscope (REMI) apparatus [8]. A pair of fused silica glass wedges is used to compensate the chirp inside the ultrahigh vacuum main chamber of the REMI. The pulse energy is adjusted by using pellicle beam splitters and precisely calibrated in situ by using the ion recoil method with circularly polarized light [9]. The pulses are directed and focused onto the supersonic gas jet of acetylene molecules using a silver coated spherical mirror of focal length $f = 7.5$ cm. The resulting ions were projected onto the position and time sensitive detectors by a weak homogeneous electric field of 30 V cm$^{-1}$. A quarter-wave plate is inserted in the beam path to change the supersonic gas jet of acetylene molecules using a silver coated spherical mirror of focal length $f = 7.5$ cm. The resulting ions were projected onto the position and time sensitive detectors by a weak homogeneous electric field of 30 V cm$^{-1}$. A quarter-wave plate is inserted in the beam path to change the polarized light into linear. The linear polarization is parallel to the time of flight axis (defined as $z$ axis) of the reaction microscope and normal to the propagation direction of the gas jet ($y$ axis) and the laser beam direction ($x$ axis). The three-dimensional-momentum vector of each fragment ion is determined by its position and arrival time on the detector plane. Two-body molecular fragmentation channels, from the ions detected in coincidence, are selected by applying the momentum conservation filter in all three dimensions. In order to securely achieve coincidence conditions, the number of generated ions per laser shot were kept $<$1 per laser pulse during the data acquisition. Measurements were taken for three different laser peak intensities ranging from $2.0 \times 10^{14}$–$9.0 \times 10^{14}$ W cm$^{-2}$ with laser polarization varying from linear to circular.

III. RESULTS AND DISCUSSION

By using coincidence momentum imaging [10], three-dimensional momentum vectors of fragment ions resulting...
from the interaction of acetylene molecules with intense few-cycle laser pulses are measured in coincidence. For all laser pulse parameters used in the experiment, three two-body fragmentation channels are identified, where acetylene dications decompose into two ionic fragments. These three two-body fragmentation channels are

\[ \text{C}_2\text{H}_2^{++} \rightarrow \text{H}^+ + \text{C}_2\text{H}^+, \quad (1) \]
\[ \text{C}_2\text{H}_2^{++} \rightarrow \text{CH}^+ + \text{CH}^+, \quad (2) \]
\[ \text{C}_2\text{H}_2^{++} \rightarrow \text{C}^+ + \text{CH}_2^+. \quad (3) \]

In (2), the C–C bond is broken without hydrogen migration, whereas the reaction pathway shown in (3) is the one in which the C–C bond is broken after the migration of one hydrogen atom from one carbon atom to the other carbon atom. Typical two-dimensional ion momentum correlation images, for linearly polarized light with laser peak intensity of \(5 \times 10^{14} \text{ W/cm}^2\), for the two-body break-up channels presented in (1), (2), and (3) are shown in Fig. 1.

In the momentum distribution of the deprotonation channel and symmetric break-up channel presented in Figs. 1(a) and 1(b), it can be clearly seen that the molecular fragmentation is preferred in the direction parallel to the laser polarization vector which is different from the previous XUV pump-probe investigation of the deprotonation channel where molecular fragmentation is favored in the direction perpendicular to the laser polarization vector [11]. This preference of laser polarization direction reflects the instantaneous alignment of the molecular ion from the randomly oriented molecules during the interaction with the short pulses that is in agreement with the recent results [12] where momentum distribution of the protons that are ejected during Coulomb explosion of \(\text{C}_2\text{H}_2^+ \geq +4\) is presented. The momentum distribution of the proton migration channel presented in Fig. 1(c) for the linearly polarized laser field is different from the other two channels and shows nearly uniform angular distribution. In the case of the circularly polarized laser field, all three two-body fragmentation channels exhibit similar isotropic momentum distribution as can be seen in Figs. 1(d)–1(f). This anisotropic behavior of the deprotonation channel and the symmetric break-up channel in the linearly polarized laser field points to the specific angular dependence of the ionization probability of acetylene. For the linearly polarized pulses of low to moderate intensity the double ionization process is dominated by a nonsequential pathway via rescattering and the overall angular dependence is defined by the angular dependence of the first ionization probability in the neutral molecule as described in [13] with an ionization yield peaking at about a 45 deg angle between the molecular axis and laser polarization. However, at the high intensities used in this study, the double ionization is dominated by the sequential mechanism and it is more probable for molecules oriented parallel to the laser polarization.

In Fig. 2, the relative yield of all three identified two-body fragmentation channels as a function of laser polarization from linear to nearly circular polarized light at three different peak intensities of laser pulse are shown. It shows that the probability of two-body fragmentation for all three channels, with the increase of intensity, is increasing. The horizontal error bars
attached to the data points originate from the uncertainties in the measured ellipticity. The errors in counts are estimated by dividing each measurement for a given ellipticity and intensity into a number of equal sections and analyzing their count statistics. That estimate accounts for all sources of fluctuations, including those in the laser intensity and gas target density. Those errors are small due to high stability of our laser and molecular gas source during the experiment. Now we focus on channels resulting from the C–C bond breaking with and without proton migration: symmetric break-up (2) and vinylidene (3) channels. As the laser polarization is changing and without proton migration: symmetric break-up (2) and focus on channels resulting from the C–C bond breaking with and molecular gas source during the experiment. Now we include those in the laser intensity and gas target density. Those errors are small due to high stability of our laser and molecular gas source during the experiment. Now we focus on channels resulting from the C–C bond breaking with and without proton migration: symmetric break-up (2) and vinylidene (3) channels. As the laser polarization is changing from linear to circular, the yield of the proton migration channel is increasing with respect to the symmetric break-up channel and relative yield of the proton migration channel at intensity $9 \times 10^{14} \text{ W/cm}^2$ and ellipticity $> 0.4$ exceeds that of the symmetric break-up channel. That has not been observed before. To understand the dependence of the proton migration channel on the laser parameters, i.e., intensity and laser polarization, a new parameter, yield ratio, is defined as $\eta$.

$$\eta = \frac{N_{p\text{-mig}}}{N_{p\text{-mig}} + N_{\text{symm}}},$$

where $N_{p\text{-mig}}$ and $N_{\text{symm}}$ are the yields of C–C bond break-up channels with a proton migration pathway presented in (3) and a symmetric break up of C–C bond without proton migration presented in (2) respectively.

In Fig. 3, the yield ratio, as defined in (4) as a function of laser ellipticity for three different intensities, is plotted.

As the laser peak intensity is increasing from $2 \times 10^{14}$ to $9.0 \times 10^{14} \text{ W/cm}^2$, the yield ratio is also increasing. In the case of linear polarization, this increase is $\sim 20\%$ from 0.36 to 0.46, whereas in the case of circular polarization the yield ratio has increased by $\sim 36\%$. The change in this ratio $\eta$ doubles from 16\% to 32\% with the increase in laser intensity from $2 \times 10^{14}$ to $9.0 \times 10^{14} \text{ W/cm}^2$. For intensity $9.0 \times 10^{14} \text{ W/cm}^2$ the yield ratio from linear to circular has increased $\sim 30\%$. It is interesting to note that while the yield ratio increases with intensity it also increases with ellipticity, even though for the same intensity higher ellipticities correspond to lower values of the peak electric field. Therefore, the effect of ellipticity is not the same trivial effect of the peak electric field, but it is a different and stronger effect which overwhelms the peak field effect acting in the opposite direction. A clear increasing tendency in the yield ratio with the change in laser polarization from linear to circular may be an indication that circularly polarized light is more efficient than linearly polarized light for inducing the proton migration. A similar laser polarization effect was observed in ultrafast hydrogen migration in methanol in an intense laser field [3]. It appears that higher intensities and more circular polarization favor production of dicaticionic states conducive of the hydrogen migration process. At these high intensities it is unlikely, though not completely impossible, that polarization-sensitive recollision excitation is to blame for such sensitivity of proton migration yield to the laser ellipticity. More probably, in the sequential ionization regime, the energy separations and transition dipole matrix elements between the specific cationic and dicaticionic states are responsible for the observed sensitivity of the relative yields to laser polarization. It should be kept
in mind that the two channels are dynamically competing with each other and with the deprotonation channel, as the separation between the relevant electronic states is relatively small and their radiative coupling to each other can be quite strong. However, based solely on these data, it is impossible to determine the particular mechanism of ionization and the source of this laser polarization effect. Nevertheless, it is clear that laser polarization is one of the factors that is affecting the ultrafast proton migration in acetylene in strong laser fields. Much more advanced and realistic theoretical modeling will be required to understand and exploit this effect more fully.

In conclusion, we experimentally investigated the dissociative double ionization of acetylene in ultrafast strong laser fields at three different intensities of various ellipticities. Three two-body fragmentation channels are identified. Our results, based on momentum distribution and fragmentation yield of the three channels, demonstrate that the deprotonation channel and the symmetric break-up channel are more favored in a linearly polarized laser fields, whereas the proton migration channel is more favored in a circularly polarized laser field. The relative yields of C–C break up into the symmetric channel and C–C break up into the proton migration channel can depend on the ellipticity of the ionizing laser field. It opens a new door to understanding the complex fragmentation dynamics of polyatomic molecules in strong laser fields.

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