Probing the Dynamics of Atoms and Molecules by High Harmonic Generation

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Abstract

In this dissertation, we have observed the phase shift of high harmonic generation (HHG) from atomic and molecular target gases by using the Gouy phase interferometric technique. The aim of this thesis is to probe the molecular structure and dynamics from the phase of emitted HHG radiation. The work mainly divided into three parts. The first part is on designing and implementing the “Advanced Gouy Phase Interferometer”. It includes the detail about the design and instrumentation that has been improvised and modified from the prototype version. The interferometer consists of two thin gas jets separable in space along the laser propagation direction in single laser focus.

The intensity of high harmonic generated pulses is modulated when the separation between two gas jets is increased. This modulation is observed due to the Gouy phase shift (which depends on the longitudinal position within the Gaussian beam) of the driving laser beam experienced by the two gas jets. The Gouy phase difference imparts a delay in HHG photon emission time. The fringes visibility or temporal coherence of several consecutive harmonic orders as a function of gas jets separation is observed with atomic Ar and molecular H\textsubscript{2} target gases. The temporal coherence properties is observed with 9 fs and 50 fs driving laser pulses. This observation of temporal coherence of the harmonics with multi-cycle driving laser pulses indicates the broader usefulness of this interferometric technique. The possible applications of this interferometer such as HHG yield enhancement, selective control of particular or range of harmonic order from the typical HHG spectrum and extracting the relative high harmonic phase shift between two gases are discussed.

In the second part, we report on extracting the relative phase shift of HHG emissions by using the advanced Gouy phase interferometric technique. As a part of this, first we measured the relative phase difference from the simplest molecular
isotopes in nature i.e., hydrogen ($H_2$) and deuterium ($D_2$). The experimental results are presented with 9 fs and 50 fs laser pulses. The results show that the relative phase shift between these isotopes increases monotonically with the harmonic order. We have observed about $180 \pm 8$ mrad phase shift for harmonic order 23 ($H_{23}$) and it increases to $230 \pm 26$ mrad for $H_{35}$ with 9 fs pulses. The experimental results agree well with the simulation results obtained by solving the non-Born-Oppenheimer time dependent Schrödinger equation. Detailed analysis of the theoretical modelling uncover the underlying mechanisms of electrons and nuclei responsible for the measured phase difference. The results indicate that the electron-ion Coulomb interaction during the electron acceleration in the continuum as well as the bound electron interaction with the ionized electron play the role on the observed phase shift. The phase shift measured with 50 fs pulses is $225 \pm 10$ mrad for $H_{23}$ and $340 \pm 38$ mrad for $H_{35}$. We anticipated that the contribution of high harmonic generated by the electron return to the higher excited $2p\sigma_u$ state of $H_2^+/D_2^+$ molecular ion along with the ground $1s\sigma_g$ state may lead to the larger phase shift with 50 fs pulses compared to the 9 fs pulses.

The final experimental result presents the HHG phase shift measurement from methane isotopes i.e., methane ($CH_4$) and deuterated methane ($CD_4$). The observed phase shift as a function of harmonic order increases at a greater rate for methane isotopes compared to the hydrogen isotopes. The measured phase shift is $95 \pm 6$ mrad for $H_{23}$ and increases to $460 \pm 83$ mrad for $H_{31}$. Theoretical analysis predicted that this phase shift comes from the difference in field free nuclear dynamics of $CH_4^+$ and $CD_4^+$ ions.
Declaration of Authorship

I, Mumta Hena Mustary, declare that this thesis titled ‘Probing the dynamics of atoms and molecules by high harmonic generation’ 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: [Signature]

Date: 11 February 2019
This work is dedicated to my parents without whom it was not possible for me to reach at this stage and my husband whose inspiration played an important role behind completing this hard work.
“If you want to understand function, study structure”.

–Francis Crick

“There is no science in this world like physics. Nothing comes close to the precision with which physics enables you to understand the world around you. It’s the laws of physics that allow us to say exactly what time the sun is going to rise. What time the eclipse is going to begin. What time the eclipse is going to end”.

–Neil deGrasse Tyson
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<tr>
<td>ATI</td>
<td>Above Threshold Ionization</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge Coupled Device</td>
</tr>
<tr>
<td>CMOS</td>
<td>Complementary Metal-Oxide-Semiconductor</td>
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<tr>
<td>CEP</td>
<td>Carrier Envelope Phase</td>
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<tr>
<td>CPA</td>
<td>Chirp Pulse Amplification</td>
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<tr>
<td>CW</td>
<td>Continuous wave</td>
</tr>
<tr>
<td>DCM</td>
<td>Dispersion Compensation Mirror</td>
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<tr>
<td>FPGA</td>
<td>Field Programmable Gate Array</td>
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<tr>
<td>FROG</td>
<td>Frequency-resolved Optical Gating</td>
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<tr>
<td>FWHM</td>
<td>Full Width Half Maximum</td>
</tr>
<tr>
<td>HR</td>
<td>High Reflector</td>
</tr>
<tr>
<td>IAC</td>
<td>Interferometric Autocorrelation</td>
</tr>
<tr>
<td>GDD</td>
<td>Group Delay Dispersion</td>
</tr>
<tr>
<td>HHG</td>
<td>High Harmonic Generation</td>
</tr>
<tr>
<td>HHS</td>
<td>High Harmonic Spectroscopy</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>KLM</td>
<td>Kerr-lens Modelocking</td>
</tr>
<tr>
<td>MCP</td>
<td>Micro-channel Plate</td>
</tr>
<tr>
<td>MPI</td>
<td>Multiphoton Ionization</td>
</tr>
<tr>
<td>NBO-TDSE</td>
<td>Non-Born-Oppenheimer Time dependent Schrodinger Equation</td>
</tr>
<tr>
<td>NSDI</td>
<td>Non-Sequential Double Ionization</td>
</tr>
<tr>
<td>OC</td>
<td>Output Coupler</td>
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<tr>
<td>OTBI</td>
<td>Over The Barrier Ionization</td>
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<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>RABBITT</td>
<td>Reconstruction of Attosecond Beating By Interference of Two-photon Transitions</td>
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<tr>
<td>SAE</td>
<td>Single Active Electron</td>
</tr>
<tr>
<td>SFA</td>
<td>Strong Field Approximation</td>
</tr>
<tr>
<td>SHG</td>
<td>Second Harmonic Generation</td>
</tr>
<tr>
<td>SPM</td>
<td>Self Phase Modulation</td>
</tr>
<tr>
<td>TSI</td>
<td>Two Source Interferometry</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra-High Vacuum</td>
</tr>
<tr>
<td>VLS</td>
<td>Variable Line Spacing</td>
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<tr>
<td>XUV</td>
<td>Extreme Ultraviolet</td>
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5.1 Comparative structural information of $CH_4$ and $CD_4$ . . . . . . . . . . 107
After the first invention of the laser in 1960 [1], this field has progressed rapidly towards shorter pulse durations and higher peak intensities. In particular, the techniques of Kerr-lens mode locking and chirped pulse amplification techniques have led to the generation of state of the art laser pulses with durations of a few femtoseconds (1 fs=10^{-15} sec), reaching peak intensities in the petawatt (1 PW=10^{15} W/cm^2) regime.

The strong field regime is the region where the amplitude of the electric field is comparable to the field strength under which an electron is bound with an atom or molecule. The interaction of intense ultrashort laser pulses with matter can lead to ionization of an electron, followed by acceleration and return back to recollide with parent ions upon reversal of laser field [2]. This recollision accompanies several interesting optical phenomena including molecular dissociation [3], non-sequential double ionization (NSDI) [4] and high harmonic generation (HHG) [5,6].

The main focus of this thesis is the HHG process that is capable of producing table-top extreme ultraviolet (XUV) light pulses. At the beginning, HHG process was limited to atomic species as a target gas and the primary goal was to increase its photon flux by improving phase matching condition and extend the cut-off energy. For more than a decade, this phenomenon has been very interesting to generate high harmonics from molecular species. HHG signal from molecular target is used to investigate the real time structural rearrangement as well as their electronic and nuclear dynamics with Ångstrom (1 Å= 10^{-10} m) spatial resolution and attosecond (1 as = 10^{-18} sec) temporal resolution.

This thesis reports on the advanced Gouy phase interferometric technique that
can extract the relative phase shift of HHG radiation generated from two different gases. This interferometer is able to produce a pair of XUV pulses from the two gas jets with a phase difference between them. This phase shift depends on the separation between the HHG generation medium along the laser propagation. The Gouy phase shift of a Gaussian beam through its focus is utilized to alter the electron recombination time and thus the photon emission time during the HHG process. The interferometer can measure with high sensitivity phase shifts between the two XUV pulses with an accuracy of few milliradians (1 mrad=10\(^{-3}\) radian). The ultimate goal of this research is observing the ultrafast dynamics and structural rearrangement of molecules after they are ionized by the strong laser field.

The first section of this chapter presents a brief overview of the progress of intense ultrashort laser physics. Section 1.2 discusses the important phenomena occurred when the intense pulse interacts with matter. The next section describes the HHG process and provides a brief history on the progress of this field. Section 1.5 gives an overview in the field of high harmonic spectroscopy that is basically the application of HHG to observe the real time dynamics properties of atoms, molecules or solids. The motivation of this dissertation is presented in section 1.6. The chapter concludes with the outline of the thesis.

1.1 Ultra-short intense laser pulses

A laser consists of an optical resonator and a gain medium within the resonator. The ultrashort laser pulse can be generated by a number of ways such as Q-switching [7], mode locking [8] and cavity dumping [9], but the technique produces fs pulses that we use is called mode-locking. In laser cavities, a large number of longitudinal modes with discrete frequencies are formed. In a continuous wave (CW) laser, the relative phase among these longitudinal modes is random (oscillate independently). In case of mode locking, each of these longitudinal modes oscillate at a fixed phase relationship with each other and constructively interfere for a very short period of time while destructively interfere all other time. A part of the energy is coupled out of the oscillator after every round trip when it hits the partially reflecting mirror (output
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Figure 1.1: Radiation power as a function of time at the output of a stationary mode-locked laser. Figure is adapted from [10].

coupler) as shown in figure 1.1. This results in a train of ultrashort pulses with a repetition rate corresponding to the round trip time in the cavity.

If $T_r$ is the round trip time of a cavity then the longitudinal modes are separated in frequency by $\frac{1}{T_r}$. The pulse duration, $\tau_p$ and peak power, $P_p$ of a mode locked laser is then defined as [10]

$$\tau_p \approx \frac{T_r}{N},$$

(1.1)

$$P_p \approx NP_{\text{avg}},$$

(1.2)

where $N$ is the number of locked longitudinal modes and $P_{\text{avg}}$ is the average output power. The equations 1.1 and 1.2 depict that for the shortest pulse duration and highest peak power, largest number of longitudinal modes need to co-exist in the laser cavity.

The mode locking technique has given birth to the field of ultrafast laser physics [11–13]. Depending on the principle of operation, mode locking can be either active [11,14] or passive [15]. Active mode locking modulates the cavity loss either by amplitude modulation or frequency modulation with an acousto-optic or electro-optic modulator. Passive mode locking is achieved by an external saturable absorber in the laser cavity. The passive mode locking technique allows shorter pulse duration compared to the active mode locking but the pulse duration is still limited to picosecond ($1 \text{ ps}=10^{-12} \text{ sec}$) due to the finite relaxation time of the saturable absorber. However, the situation changed in early 1990s after the realization of self-focusing in laser gain medium that coupled with an intra-cavity aperture and
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act like a near instantaneous saturable-absorber. This effect is known as Kerr-lens mode locking. More detail about the progress in the field of ultrashort laser physics can be found in the review articles [10, 16, 17].

1.1.1 Kerr-lens mode locking

Kerr-lens mode locking (KLM) [18] is a passive mode locking technique that creates an artificial saturable absorber in the laser gain medium with non-linear optical Kerr effect [19]. The Kerr effect is a nonlinear optical effect where the refractive index of material is modified in response to incident radiation intensity and can be represented by the relationship [20]

\[ n(I) = n_0 + n_2 I(r, t) \]  

(1.3)

where \( n(I) \) is the refractive index of the optical material, \( n_0 \) linear refractive index present at low intensities, \( I(r, t) \) is the laser intensity and \( n_2 \) is material dependent non-linear refractive index. At low intensities the second term of equation 1.3 is negligible. The nonlinear refractive index for Ti doped sapphire is \( 3.18 \times 10^{-16} \text{cm}^2/\text{W} \) [21] thus its influence can become significant in strong light fields. For a Gaussian beam, the spatial profile of the intensity can lead to self-focusing when \( n_2 > 0 \) as the centre of the beam is more intense than the outside. Thus the Kerr effect modifies the medium to look like a positive focusing lens [22] as shown in figure 1.2 and the aperture allows high intensity pulsed beam pass through. The transverse gain profile of the laser cavity can be altered in favour of self-focusing by resonator geometry so the aperture is not necessary in practice. The Kerr-effect is instantaneous that gives very fast response to the effective saturable absorber. As a results pulses as short as few fs can be achieved by KLM technique.

1.1.2 Chirp pulse amplification

Although pulses as short as \( \sim 10 \text{ fs} \) were able to be produced with the advent of KLM and dispersion compensation by prism pairs [23–25], the peak intensity was still limited to \( \text{GW/cm}^2 \). This is because, if the laser pulse of \( \text{GW/cm}^2 \) intensities directly send into the optical gain medium for amplification, the self focusing onto the
Figure 1.2: The working principle of Kerr lens mode-locking technique. The self focusing in the non-linear medium is more for intense pulses than it is for CW. Figure is reproduced from [10].

gain medium can lead to material damage. High fluence (energy/area) is necessary to extract maximum energy but high intensity (power/area) is not acceptable as self focusing effects are induced at high intensities. Thus, it is important to decouple pulse fluence and intensity. This problem was solved after the introduction of chirp pulse amplification (CPA) technique in 1985 by Donna Strickland and Gerard Mourou [26, 27] who were awarded the Nobel prize in physics in 2018 for this remarkable invention. Figure 1.3 shows the schematics of CPA technique that involves the following three steps:

1. Before passing through the gain medium, the fs duration pulse is temporally broadened (stretched) in the order of $10^3 - 10^5$. Pulse broadening is achieved by introducing a large amount of chromatic dispersion by means of a dispersion element (i.e., grating or prism) and expands the pulse duration from fs to ps or even longer.

2. The stretched pulse is then sent into the gain medium for amplification. Due to the long pulse duration, the peak power now is not high enough to cause any detrimental nonlinear effect in the gain medium.

3. The amplified pulse is then compressed back to retrieve the original pulse duration as it was before stretching.

The laser system that has been used for the experiments in this thesis works based on KLM and CPA techniques by using Ti:Sapphire crystal as an optical gain medium. The detail about the laser system will be discussed in chapter 2.
1.2 Intense light-matter interaction

With the development of mode-locking and chirp pulse amplification techniques, state-of-art laser technology can produce pulses as short as few fs and if it is confined in space (by focusing the beam) the peak intensity can reach to $10^{14} \text{W/cm}^2$ or higher. The electric field strength at this intensity is comparable to the Coulomb interaction experienced by the outer shell electron in an atom or molecule. For instance, the binding electric field of hydrogen atom is $5.2 \times 10^9 \text{ V/cm}$ (equivalent to the electric field of a light pulse with an intensity of $3.5 \times 10^{16} \text{ W/cm}^2$). A laser field with this intensity can significantly perturb the electron-nucleus interaction. In strong field physics, depending on the ionization potential of atom and molecule, intensity and wavelength of the laser, several ionization pathways are possible. Keldysh was the first person to classify different ionization regimes by introducing an adiabaticity parameter [29] that gives us an idea of which ionization pathway is likely to dominate.
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This parameter is called Keldysh parameter, \( \gamma \) and is defined as,

\[
\gamma = \sqrt{\frac{I_p}{2U_p}}, \tag{1.4}
\]

where \( I_p \) is the ionization potential energy of an atom or molecule and \( U_p \) is the cycle averaged kinetic energy (or ponderomotive energy) that an electron gain during acceleration in the continuum with the influence of laser field. The ponderomotive energy is defined as

\[
U_p(eV) = \frac{e^2 E^2}{4m_e \omega^2}
\]

\[
\propto 9.33 \times 10^{-14} I(W/cm^2) \lambda^2(\mu m) \tag{1.5}
\]

where \( I \) is the intensity of the laser field and its relationship with the electric field, \( E = \sqrt{\frac{2I}{\epsilon_0 c}} \), \( c \) is the speed of light, \( \epsilon_0 \) is the permittivity in free space, \( \omega \) is the angular frequency and \( \lambda \) is the wavelength of the laser radiation.

There are mainly three different pathways which lead to ionization of an atom or molecule includes multiphoton ionization (MPI) [30], tunnel ionization [29] and over the barrier ionization (OTBI) [31]. For a particular atom, laser intensity and wavelength determine which pathway will dominate. This section discusses these different ionization pathways.

1.2.1 Multiphoton ionization

Multiphoton ionization occurs at weaker laser field when \( \gamma >> 1 \), i.e. ionization potential is greater than ponderomotive energy. Multiple photons are absorbed simultaneously by the outer shell electron to push it to the continuum as shown in figure 1.4 (a). If the number of photons multiplied by the energy of each photon is greater than the ionization potential, the electron is freed. The probability of MPI decreases if the required number of photon increases. The ionization rate scale with intensity as a power law as [32]

\[
\Gamma_n^{MPI} = \sigma_n I^n, \tag{1.6}
\]
where $\sigma_n$ is the $n$-photon absorption cross-section and $I$ is the laser intensity. The minimum energy that a released electron may gain is $E = n\hbar\omega - I_p$, with $n$ being the minimum number of photons required to overcome the binding energy of the atom. In addition to this, above threshold ionization (ATI) is an unexpected form of multiphoton effect where photons being absorbed by an already ionized electron. The excessive number of photon energy added to the kinetic energy of the released photon.

### 1.2.2 Tunnel ionization

Tunnel ionization dominates at higher laser intensities corresponding to $\gamma << 1$ and when the field strength is comparable to the inner atomic electric field (Coulomb potential). The electric field strength deforms the Coulomb potential and finite barrier is established so that bound electron can tunnel through the barrier in the continuum as shown in figure 1.4 (b). The tunnel ionization rate depends exponentially with ionization potential and detail about it will be explained in the high harmonic generation section.

### 1.2.3 Over the barrier ionization

Over the barrier ionization happens at even higher laser intensities than the tunnelling regime where the potential barrier is lowered to the level below the bound state and the electron can leave the atom over the barrier. This phenomenon known as over-the-barrier ionization.

Generally, $\gamma << 1$ for tunnel ionization while $\gamma >> 1$ for MPI. However, it should be noted that the contribution from all regimes is possible at different intensities and the choice of the particular regime is quite ambiguous for intermediate $\gamma$ values. For example, at $\gamma \geq 1$ electron can interact with laser field classically forbidden region and allowed region and thus there can be a peaceful co-existence between tunnel ionization and multiphoton ionization.
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1.3 High harmonic generation

Laser produced coherent light has revolutionized the atomic and molecular physics research and thus the motivation to produce high energy shorter wavelength laser is increasing over the years. However, producing shorter wavelength laser is difficult because of several reasons. Light at XUV or soft X-rays regime is highly absorptive in material. In addition, manufacturing the optics suitable for these wavelengths is expensive and challenging. Besides, the required power to initiate lasing scale as \( \lambda^{-4} \) with wavelength [33] that demand for high power pump sources. Currently, the most prominent laser source in XUV and soft X-ray region is synchrotron light source and free electron lasers that are highly expensive which generally have low accessibility to the facility.

HHG is an extremely non-linear optical phenomenon first observed in 1987 [5,6]. It provides an excellent source of table-top coherent radiation in the wavelength region extended to XUV and soft X-ray. The origin of this phenomenon is the interaction of strong laser field with matter (gas, liquid, solid or plasma). However, we will limit our discussion with gas medium as experiment presented in thesis based on gaseous target.

An interesting feature about HHG photon is its temporal characteristics. The
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HHG process occurs every half of a driving laser optical period (2.7 fs for 800 nm laser) that make it possible to produce train of attoseconds pulses \[34\] and single attosecond pulses \[35\]. For the last more than a decade HHG has become a very interesting technique to probe the real time atomic and molecular dynamics. In this section, we will discuss about the microscopic and macroscopic aspects of HHG process.

1.3.1 Microscopic single atom response (Three-step model)

The basic principle of HHG can easily be understood by an intuitive simple man model or three step semi-classical model \[2, 36\]. The three step model of HHG is shown in figure 1.5. This three distinct sequential steps involve: (i) The strong laser field suppresses the binding Coulomb potential feel by the outer shell electron of an atom or molecule. Thus, an electron is ionized from the ground state to tunnel through the barrier with zero velocity. (ii) After tunnelling, electron motion is treated as a free particle by a classical picture. The electron accelerates away from parent ion following the newton’s second law of motion \( F = ma \) driven by the oscillating laser field. (iii) After a certain time delay, the electron returns back and recollides with its parent ion upon reversal of the field direction. There are four possible consequences that can be happened during this recollision process \[37\]:

1. Energetic electron rescattered elastically from the parent ion.
2. Ionization of another outer shell electron called non-sequential double ionization.
3. Excitation of other bound electrons by inelastic collision.
4. Recombination with its ground state and emission of an high energy photon results in high harmonic generation.

Here, we will discuss briefly each of these three steps of high harmonic generation.

Ionization

As we have discussed in section 1.2, for a particular target atom, depending on the laser frequency and field strength, different ionization pathways are possible and tunnel ionization is one of them. In the strong field regime, when the peak intensity
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of laser pulse reaches to $10^{14} \text{ W/cm}^2$ and Keldysh parameter $\gamma << 1$, potential barrier of an atom is suppressed and an electron undergoes for tunnel ionization. The probability of tunnel ionization is the highest near the peak of laser electric field as the tunnelling rate is exponentially dependent on the field strength as shown in equation 1.7. Ionization rates from atoms and atomic ions can be computed from the ADK model developed by Ammosov, Delone and Krainov [38]. According to this model, the probability of ionization from the ground state is calculated as a function of laser and atomic parameters as (in atomic units)

$$\omega(t) = |C_{n^*l^*}|G_{l^*|m|}I_p \left( \frac{2(2I_p)^{3/2}}{E(t)} \right)^{2n^*-|m|-1} \exp \left( \frac{-2(2I_p)^{3/2}}{3E(t)} \right) \tag{1.7}$$

where $l$ and $m$ are the angular and magnetic quantum numbers of the outermost electron of the atom, $I_p$ and $E(t)$ are the ionization potential and instantaneous electric field amplitude respectively. The two coefficients $C_{n^*l^*}$ and $G_{l^*|m|}$ are the atomic parameters that depend on the quantum numbers $l$, $m$ and effective quantum numbers $n^* = Z/\sqrt{(2I_p)}$, $l^* = n^* - 1$, where $Z$ is the effective nuclear charge.

**Acceleration**

During acceleration, the electron in the continuum behaves as a free particle and its trajectory is driven by the oscillating laser field. In semiclassical model of HHG, the electron motion is considered to be dominated only by the laser field. It considers two approximations: firstly, single electron approximation (SAE) where only one electron is ionized and others are screened in the nucleus. Secondly, strong field approximation (SFA) where Coulomb force on the ionized electron during acceleration is negligible. The average kinetic energy gained by the electron during acceleration is called the ponderomotive energy, $U_p$.

In fact, electron motion during acceleration in the continuum depends on the phase of the laser field when ionization occurs. Generally, two electron trajectories (short and long) contribute to each HHG photon energy as shown in figure 1.6. The ionization and recombination phase (or time) of short and long trajectories are different but their return energy to the core are the same that leads to harmonic
Figure 1.5: Single atom microscopic picture: three step model of HHG. (a) A classical schematic: An electron from an atom tunnel ionized by the intense laser field. Then the electron accelerates away from parent ion and gain energy driven by the laser field. After a certain time delay, it returns back to the ground state of the same atom and if recombine it emits energy as a high-energy photon. Figure is adopted from [39]. (b) The quantum mechanical perspective: Ionization splits the wavefunction into two; a part of wavepacket tunnel out of the barrier that behaves as a free electron in the optical field and another part remains as localized electron with the parent ion. The laser field drives the electron wavepacket and when it returns to parent ion these two wavefunctions overlap. The resulting dynamic interference pattern transfers the kinetic energy, amplitude and phase from the recollision electron to the XUV photon generated from HHG. Figure adopted from [40].
radiation of same frequency. The motion and kinetic energy of the electron can be calculated from the classical equation of motion. Consider a linearly polarized laser electric field as

\[ E(t) = E_0 \cos(\omega t), \]  

(1.8)

where \( E_0 \) is the maximum electric field amplitude and \( \omega \) is the angular frequency. The force acting on the electron (after it is freed) by this field is

\[ m_e a(t) = -eE_0 \cos(\omega t), \]  

(1.9)

where \( m_e \) and \( e \) are the mass and charge of the electron and \( a(t) \) is the instantaneous acceleration. Then, the velocity of electron is

\[ v(t) = -\frac{eE_0}{m_e \omega} \left[ \sin(\omega t) - \sin(\omega t_i) \right], \]  

(1.10)

and time dependent displacement of the electron is

\[ x(t) = \frac{eE_0}{m_e \omega^2} \left[ \cos(\omega t_i) - \cos(\omega t) - \omega(t - t_i) \sin(\omega t_i) \right], \]  

(1.11)

here \( t_i \) is the ionization time when electron motion start from \( x = 0 \) and \( t - t_i = t_r \) is the electron recombination time when returns to \( x(t > t_i) = 0 \). The kinetic energy of the electron associated with velocity is

\[ E_{kin} = \frac{1}{2} m_e v^2 = 2U_p \left[ \sin(\omega t) - \sin(\omega t_i) \right]^2. \]  

(1.12)

### Recombination

The final step of HHG process is the recombination of the ionized electron with its parent ion followed by the emission of a photon. The energy of the emitted photon upon recombination is determined by the sum of the ionization potential \( I_p \) and the electron kinetic energy \( E_{kin} \) gain during acceleration in the continuum [41]

\[ E_{XUV} = \hbar \omega = I_p + E_{kin(\phi)}, \]  

(1.13)
here $\phi$ is ionization phase of the electron. This ionization phase/time determines the recombination phase/time as well as the kinetic energy that the electron will gain. The maximum kinetic energy an electron can achieve is given by

$$E_{\text{cutoff}} = \hbar \omega_{\text{max}} = I_p + 3.2 U_p.$$  (1.14)

The cut-off energy can be extended by using higher $I_p$ target material or increasing the driving laser wavelength and intensity. However, higher intensity can deplete the medium at the rising edge of a multicycle laser pulse. In addition, if the intensity of the driving laser exceeds $10^{16} W/cm^2$, the magnetic field force can no longer be neglected. As a result, the induced Lorentz force $\vec{v} \times \vec{B}$ drives the electron motion significantly in the field of laser propagation and electron may gain velocity of the order of light that prevents its return to the parent ion. Therefore, the possibility of electron to return to its parent nucleus is reduced and HHG radiation is suppressed [41, 42].

**Harmonic spectrum**

Figure 1.7 illustrates a typical frequency spectrum of high harmonic radiation. Three distinct regimes are observed in the typical HHG spectrum. A sharp decrease of harmonic intensity at lower order harmonics produced at the leading and trailing edge of the driving laser pulse where intensity is comparatively low. This part can be described by perturbation theory, predicting a decrease of harmonic intensities towards higher orders by $I^q$ power law. Next, the non perturbative plateau region where harmonic intensities are approximately equal with the increasing order. These harmonics are produced at high laser field strengths and both electron trajectories (short and long) contribute to the high harmonic spectrum. These two trajectories have different ionization phases but same kinetic energy leading to the emission of the same frequency. After the plateau, there is a cut-off region where the intensity of the harmonics drops sharply. The maximum cut-off energy depends on the ionization potential and laser intensity and frequency according to the equation 1.14.

The HHG or a burst of XUV radiation is generated at every half cycle of the driving laser pulse. Thus, for multicycle laser pulse this process is repeated periodically and
Figure 1.6: (a) Electric field of an optical cycle. (b) Classical calculation of electron kinetic energy in unit of $U_p$ as a function of ionization and recombination time in one optical cycle of laser field. The blue points represent the ionization time, whereas the red points are for recombination time. The long and short trajectories have different ionization and recombination times (phases) but their return energies are same that can give the same HHG photon energy for both of these trajectories.
Figure 1.7: A typical HHG spectrum. It can be divided into three distinct regions: perturbative region at lower orders where intensity decreases exponentially with harmonic order, a plateau with similar intensities for a range of harmonic order and the cut-off region at higher orders where harmonics intensity decreases rapidly. Figure is adapted from [41].

A train of subfemtosecond XUV pulses are emitted at every half optical cycle in the time domain. In the spectral domain, this corresponds to a comb with a $2\omega$ spacing of driving laser. In addition, consecutive XUV bursts result from the collisions of electron from alternating directions and the spectral components have the same amplitude but differ in sign. For centrosymmetric material, this leads to destructive interference for even-order harmonics ($\omega_q = 2m\omega_L$), while constructive interference for odd order harmonics ($\omega_q = (2m + 1)\omega_L$) [41]. This inversion symmetry on positive and negative half cycle results in only odd order harmonic to be observed. However, this symmetry can be broken and even order harmonic can be observed in an oriented asymmetric medium as a generating source [43], single cycle regime laser pulse [44] and two color laser field [45].

1.3.2 Macroscopic response (Propagation effects)

The typical HHG spectrum shown in figure 1.7 is considering a single atom response with the laser field. However, it does not completely explain the HHG process in the medium. In practice, propagation effects play an important role on the experimentally observed HHG yield and spectral shape. The high harmonics are generated individually from a large number of atoms or molecules and the HHG signals are added up coherently for efficient conversion efficiency. Figure 1.8 illustrates
how the harmonic emissions from individual atoms are coherently added together.

The propagation effects due to the presence of a neutral atom or free electrons in the dispersive medium can cause significant spatiotemporal distortion on the emitted harmonics. This causes one of the major drawbacks of attosecond physics which is low photon flux (HHG conversion efficiency) that mainly comes from the phase mismatching [46–49] and photo-reabsorption of the HHG photon. The phase velocity of fundamental infrared (IR) pulses in the gas medium is slower than the generated XUV pluses because of the dispersion. To obtain strong HHG emission in the macroscopic medium, the wave-front of the fundamental IR laser and XUV pulses need to be in phase such that HHG radiations from many atoms in the medium added up coherently. The phase mismatch between driving laser and high harmonic emission is expressed as,

$$\Delta k = qk_0 - k_q,$$

(1.15)

where $k_0$ and $k_q$ are the wave vector for fundamental IR beam and $q^{th}$ harmonic respectively and $q$ is the harmonic order. For perfect synchronization condition, total phase mismatch, $\Delta k$ need to be zero. The distance over which the IR wave front and the harmonic wave front become out of phase ($\pi$ phase shift) is called the coherence length,

$$L_c = \frac{\pi}{\Delta k}.$$

(1.16)

In general, macroscopic phase mismatching depends on four different terms and is expressed as [49, 50]

$$\Delta k_q = \Delta k_{neutral} + \Delta k_{plasma} + \Delta k_{geometric} + \Delta k_{dipole},$$

(1.17)

1) The first term is the phase mismatch due to the material dispersion (positive phase) in neutral gases and occurs because of the refractive index difference between IR and XUV pulses.

$$\Delta k_{neutral} = \frac{2\pi q}{\lambda} P(1 - \eta)(n_{laser} - n_q),$$

(1.18)

here $\lambda$, $\eta$ and $P$ are the fundamental laser wavelength, ionization fraction and gas pressure, respectively. $n_{laser}$ and $n_q$ are the refractive index of IR and $q^{th}$ harmonic,
respectively. Usually neutral dispersion is not significant unless at very high gas density.

2) The second term of equation 1.17 is the phase mismatch due to the plasma dispersion (negative phase) occurring because of the refractive index difference between plasma and HHG radiation. During the interaction of the laser pulse with target gas, not only high harmonics are emitted but also free electrons are generated that lead to plasma dispersion. The phase mismatch due to plasma dispersion is expressed as,

\[ \Delta k_{\text{plasma}} = \eta PN_{\text{atom}} r_e \lambda (q - \frac{1}{q}), \]  

(1.19)

where \( N_{\text{atom}} \) and \( r_e \) are the atomic number density and electron radius, respectively.

3) The geometrical phase mismatch mainly comes from focusing geometry named Gouy phase. When a Gaussian beam passes through the focus, its phase velocity changes with the carrier wave due to the change of wavefront curvature compared to the plane wave. This leads to a phase mismatch called Gouy phase shift. The geometric phase mismatch of XUV pulses of \( q^{th} \) harmonic order due to the Gouy phase shift, \( \phi_{\text{Gouy}} \) is expressed as

\[ \Delta k_{\text{geometric}} = q\phi_{\text{Gouy}}. \]  

(1.20)

4) Dipole phase mismatch is an intrinsic phase and related to the quantum paths (short or long trajectories) of the ionized electron involved in HHG. The dipole phase is accumulated by the ionized electron during its propagation in the continuum under the influence of oscillating laser field before recolliding with parent ion. The sign of dipole phase is not fixed because it varies linearly with the laser intensity.

In gas jet geometry, the intensity dependent dipole phase and Gouy phase are the dominant terms while in gas cell or hollow fiber geometry, the neutral and plasma dispersion terms dominate. By balancing these four types of phase mismatch we can increase the conversion efficiency of the HHG signal [51,52].
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Figure 1.8: Macroscopic phase-matching of HHG in the spatial domain. For phase-matching harmonic emissions from many atoms over an extended medium (of length $L_{\text{medium}}$) need to be added coherently. Figure is adopted from [39].

Photoreabsorption

Reabsorption is another factor that plays an important role to limit the conversion efficiency of HHG radiation. The HHG signal improves with increased interaction length and gas pressure. However, at the same time, if the harmonics are propagated through the gas medium with no new harmonic generation, the signal will degrade exponentially with the interaction length and gas pressure due to reabsorption [53]. Photoreabsorption of HHG pulses becomes significant in a gas filled cell or hollow fiber medium geometry.

The HHG experiments present in the thesis are not aimed to maximize the photon flux of XUV pulses. However, phase-mismatching effects is minimized here by using a gas at low pressure with a short interaction length (thin gas jet and focus the beam close to the jet tip) compared to the Rayleigh range of the driving laser beam. Thus, the phase mismatch due to the neutral and plasma dispersion are considered to be minimized.

1.4 Brief history of high harmonic generation

Shortly after the invention of the laser in 1960 [1], Peter Franken et al., in 1961, observed second harmonic generation (SHG) by focusing the light from a Ruby laser (at 694 nm) into an isotropic crystalline quartz sample [54]. This was a breakthrough
in the field of nonlinear optics although the full impact was not realized as the SHG spot was removed from the original publication considering the dim spot (at 347 mm) as a speak of dirt. In 1967, the first third order harmonic generation was demonstrated in a gas medium [55]. However, this upconversion of light to shorter wavelengths was considered as perturbative (weak field) regime where non-linear medium is not damaged and conversion efficiency decreases rapidly with increasing harmonic order. The situation changed in 1987 when McPherson et. al. observed up to 17\textsuperscript{th} harmonic order from interacting \textit{KrF} excimer laser pulses with neon gas [5] and later a range of successive harmonics with comparable intensity (plateau) over many orders was observed [6, 56]. These pioneering experiments necessitated the non-perturbative understanding of non-linear optics.

Hereafter, numerous number of theoretical works were developed to understand the physics of the HHG process by semiclasical models [2,36,57] and quantum mechanical explanations based on SFA model [58,59]. At the same time, experimentalists made tremendous efforts to extend the HHG cut-off energy by using higher ionization potential target gas, the driving laser intensity and wavelength. For example, L’Huillier et al. observed the 29\textsuperscript{th}, 57\textsuperscript{th} and 135\textsuperscript{th} harmonic order with \textit{Xe}, \textit{Ar}, and \textit{Ne} gas respectively by using a Nd:glass laser with a wavelength of 1053 nm and pulse duration of 1 ps [60]. In addition, the conversion efficiency or photon flux [61,62] of the produced HHG signal is enhanced for future applications. Another promising aspect of HHG is the capability of producing a train of attosecond pulses [34] and single attosecond pulse [35].

1.5 High harmonic spectroscopy

One of the major goals of the experimentalists in physics, chemistry and biology is the real time observation of structure and dynamical changes in matter when it undergoes chemical processes. However, the temporal and spatial resolution of atom/molecules is a challenge to achieve this goal. High harmonic generation is not only a source of coherent table-top extreme ultraviolet light but also a promising field to encode the properties (dynamical information and charge rearrangement)
of the generating atom/molecules while interacting with a strong laser field. The
initial interest about HHG was only on increasing the conversion efficiency and
generating attosecond pulses from atomic gas species. For the last more than a
decade, molecular spectroscopy from HHG emission has attracted researchers for
real time imaging of molecular dynamics. This section will give a brief overview on
high harmonic spectroscopy (HHS) that deals with imaging of atoms and molecules
from high harmonic emission. More detail about HHS will be found in the review
articles [63–65].

High spatial resolution is indispensable for clear imaging of an object while
high temporal resolution is crucial for capturing the image of a moving particle.
Figure 1.9 represents the length and time scale of electrons in atoms, molecules and
nanostructure. The typical space and time scales of electrons in atom and molecule
are angstroms ($0.53 \times 10^{-10}$ m for hydrogen atom) and attoseconds ($24 \times 10^{-18}$
sec for hydrogen atom) respectively. For decades, researchers have been developing
tools to image electronic and nuclear motion in matter. High spatial resolution can
be achieved by crystallography from synchrotron radiation or scanning tunnelling
microscopy, and high temporal resolution by accelerated ion collision.

However, the phenomenon that can combine both of these resolutions is HHG.
These resolutions comes from the three step process of HHG itself. That is why it is
called the self-probing of molecules or a molecule is probed by its own electron [65]. In
this scheme, the amplitude and phase of emitted HHG photons provide the molecular
structural and dynamical information. Details about different scattering mechanism
about this paradigm can be found in review articles [63, 65]. The self-probing
corresponds to a pump-probe scheme where the ionization step of HHG is considered
as pump and recombination (inelastic electron ion scattering) as probe as shown
in figure 1.10. In the intermediate step (propagation/acceleration), an electron
wavepacket is formed in the continuum whose central wavelength and evolution time
perfectly match with the spatial and temporal resolutions of molecules. This electron
wavepacket takes the role of probing the molecular at the moment of recombination.
This advantage of high resolution comes from the different dispersion relationship of electron wavelength compared to photon wavelength. Electrons can reach Ångstrom scale at much lower energy compared to photon energy [65]. The de Broglie wavelength of an electron is given by

$$\lambda_e = \frac{2\pi}{\sqrt{2E_e}}, \quad (1.21)$$

and the wavelength of photon is

$$\lambda_p = \frac{2\pi c}{E_p}, \quad (1.22)$$

where $E_e$ and $E_p$ are the electron and photon energy respectively. For example, the kinetic energy of an emitted HHG photon from 10 to 100 eV corresponds to a de Broglie wavelength from $3.9 \times 10^{-10}$ m to $1.22 \times 10^{-10}$ m, latter one is close to size of a diatomic molecule [64]. Thus, it is the de Broglie wavelength of recolliding electron wavepacket that gives the high spatial resolution.

The subfemtosecond temporal resolution comes from the duration over which electron travels in the continuum between the ionization and recombination. This duration is determined by the driving laser optical cycle. For example, the oscillation period of one optical cycle for 800 nm wavelength laser pulse is 2.7 fs. As HHG process occurs in half of an optical cycle so the delay (time during which the electron wavepacket in the continuum and ground state wave-function evolved) between electron ionization and recombination is in the order of $\sim 1$ fs. In addition, since the recollision occurs in a well synchronized manner for consecutive harmonic orders (almost linear with recollision time to energy) a one to one mapping of the recollision time (atto-chirp) to the energy is possible. The delay between return time of consecutive harmonics is 100 as [66, 67] every harmonic contribute as a frame of molecular movie at attoseconds resolution and the film last for $\sim 1$ fs.

The amplitude, phase and polarization of the emitted HHG photon is very sensitive to the state and shape of the molecular ion at the moment of recombination. To date, there are several approaches that have been taken by researchers to image
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Figure 1.9: Spatial and temporal scale electron, atom and molecule. Figure is adopted from [37].

the molecular structure and dynamics by HHS that will be discussed briefly in this section.

Structural information from aligned molecules

Atoms are isotropic system so the ionization and recombination do not depend on the angle of laser polarization. However, HHG in molecular media is much more complex and interesting due to the additional nuclear vibrational and rotational degrees of freedom. Observation of molecular structural information from aligned molecules has been successfully demonstrated with high temporal resolution both theoretically and experimentally [69–72].

By solving the time dependent Schrödinger equation for $H_2$ and $H_2^+$ Lein et al. have found a characteristic amplitude minimum in the harmonic spectrum for an angle $\theta$ between laser polarization and molecular axis [69]. This spectral minimum is due to the dipole amplitude from the two atomic centres of the molecule (two center interference) when the internuclear separation is half of the de Broglie wavelength of the returning electron. The phenomenon has later been experimentally verified by Baker et al. [67]. The condition for constructive and destructive interference of the
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Figure 1.10: Probing molecular dynamics by the correlated electron wavepacket. Figure is adopted from [68].

harmonic spectrum corresponds to

\begin{align*}
R \cos \theta &= n \lambda_B, \quad (1.23) \\
R \cos \theta &= (n + \frac{1}{2}) \lambda_B, \quad (1.24)
\end{align*}

where \( R \) is the internuclear separation, \( \theta \) is the angle between molecular axis and laser polarization direction, \( n \) is the minimum or maximum order and \( \lambda_B \) is the de Broglie wavelength of the returning electron. The HHG spectrum was studied from linear \( CO_2 \) molecules as a function of angle \( \theta \) between laser polarization and molecular axis [72]. A minimum yield was found for all harmonics at \( \theta = 0 \), while a maximum HHG yield for different harmonic order from alignment angle between 0° to 90°. A pioneering work by Paul Corkum’s group in Ottawa tomographically reconstructed the highest occupied molecular orbital (HOMO) from aligned \( N_2 \) molecules [70].

Nuclear dynamics: by chirp encoded recollision

Another interesting experiment of HHG spectroscopy is observing nuclear dynamics in a fraction of their vibration motion by chirp encoded electron re-collision [66–68,73]. The short time interval between the ionization (pump) and recombination (probe) and intrinsic chirp of recombining electron wavepacket of HHG is the basis of this principle. It was first proposed by Niikura et al. originally studied for excitation and subsequent dissociation of \( D_2^+ \) [68,74]. Usually the nuclear vibration occurs
in 10 fs which is too long compared to the electron return time after ionization. The excursion time of electron during HHG process in the continuum are different for different harmonic order and it is almost linear with the harmonic order. The resolution of the return time between consecutive harmonic orders is 100 as. By using this technique a nuclear movie can be made in 100 as resolution. The pump probe delay can be adjusted by controlling two parameters; driving laser laser intensity and wavelength.

The theoretical studies from hydrogen and water isotopes predicts that the HHG signal depends on the faster or slower nuclear motion of the isotopes. Later it experimentally verified and probed nuclear vibrational motion by comparing the HHG intensity from the $H_2/D_2$, $CH_4/CD_4$ and $NH_3/ND_3$ molecular isotopes [66,67,73].

Nuclear dynamics: other pump probe schemes

There are other experiments to observe the vibrational and rotational motion of the nuclei by different types of pump probe schemes. For example, the vibrational wavepacket of the $SF_6$ molecule is excited with a short pulse in an impulsive stimulated Raman process and a delayed intense probe pulse generates harmonics. The oscillation of the harmonics was observed for different delays between the pump and probe pulse and the result indicates the relaxation dynamics of the molecule [75]. A similar kind of experiment was implemented for $N_2O_4$ dimers where a weak pump pulse excites the ground state vibrational state and a strong IR pulse generates harmonics. Other pump probe experiments using HHS investigated the rotational motion from aligned $O_2$, $CO_2$ and $N_2$ molecules [71,76,77].

1.6 Motivation

In the late 19th century, pioneer photographer Eadweard Muybridge took multiple images of a horse during a complete one period of its gallop. He arranged many threads along a race track of the horse gallop and connected a camera with each of these threads which took a picture when the thread was pulled. When the horse ran along the track of the gallop, it hit the tread and images were captured during
Chapter 1. Introduction

Figure 1.11: Eadweard Muybridge photopgraph of a horse gallop [78].

a different part of the horses gallop. These images answered the question whether all four feet of a horse are in the air at any moment during its gallop [78], which was certainly not possible to see by human eye. In the mid 20th century, Harold Eugene Edgerton took flash photography of a bullet going through an apple or air balloon to observe how the object breaks [79]. He took very nice images and unravel various incidents occur in microsecond timescale. Today, science has developed tremendously and modern electronic cameras can take images on the order of ps resolution. However, if we need to go further we have to move into optical flash light.

In atoms and molecules, any physical and chemical changes, i.e., structural deformation and reconstruction, electronic and nuclear motions occur on the fs and as timescales. With the development in laser physics, pulses as short as few fs are accessible and it is even possible to generate as pulses via the HHG process. The emerging experimental and theoretical investigation on light-matter interaction in strong-field regime opened up new directions to observe the real-time electronic and nuclear dynamics in atoms and molecules such as electron tunnelling time, nuclear vibrational dynamics, molecular fragmentation and dissociation.

The recombination process of HHG provides the snapshot of the dynamics and
structure of the target medium (atom or molecules) on the amplitude and phase of the emitted high harmonic radiation. Thus, in order to get the full information about the target medium both intensity and phase is important to know. Generally, detectors are only sensitive to the intensity of light. That is why most of the experiments on HHG observe the molecular dynamics from high harmonic intensity measurement. Interferometry is the most common approach to observe the phase shift of light but building a direct interferometric technique in the XUV regime is technically challenging, in particular to impart the delay precisely with the current interferometric techniques.

The Gouy phase interferometric technique exhibits 100 zeptoseconds (1 zs=10^{-21} sec) resolution to impart the delay between two XUV pulses generated by a single driving laser pulse. We measured the relative high harmonic phase shift between hydrogen and methane isotopes by using this interferometric technique.

1.7 Outline of the thesis

This dissertation focuses on a newly developed XUV interferometry called the Gouy phase interferometer and extracting the relative phase of HHG emission between isotopes using this interferometric technique. The thesis outline is presented below:

Chapter 2 describes the detail of the apparatus used for the experiments presented in this thesis. At the beginning, each part of the laser system that delivers the ultrashort laser pulses is described. Later, the apparatus of the advanced Gouy phase interferometer is presented. Finally, details of the high harmonic generation and detection section is discussed.

Chapter 3 provides the introduction and working principle of the Gouy phase interferometer. The phase shift between the two XUV pulses generated in two gas jets of the interferometer upon gas jet separation is presented. The temporal coherence of the consecutive harmonic orders generated from atomic and molecular gases is observed. The applications of this interferometric technique with experimental results
are also discussed. Finally, the phase resolution of the interferometer is estimated.

Chapter 4 represents the measurement of the relative phase shift of HHG emissions from hydrogen ($H_2$) and deuterium ($D_2$) isotopes. The derivation of relative HHG phase shift between two gases and measurement protocol by using the advanced Gouy phase interferometric technique is explained. The experimental results with 9 fs and 50 fs driving laser pulse is presented. The experimental data is validated with theory by solving the non-Born-Oppenheimer time-dependent Schrödinger equation.

Chapter 5 presents the HHG phase shift between more complex hydrocarbon molecular isotopes; i.e., methane ($CH_4$) and deuterated methane ($CD_4$). The experimental result is compared with numerical simulation as well.

Chapter 6 summarizes all the experimental results presented in this thesis and provides some future directions for this work.
This chapter provides a brief description about the apparatus that is used for the experiments presented in this thesis such as HHG and measuring the phase shift of HHG between two isotopes using the Gouy phase interferometric technique. The high intensity ultra-short laser pulses is the basic requirement to generate higher order harmonics. The chapter begins with the description of a Ti:Sapphire based ultra-short laser system. Next, pulse characterization techniques and methods to estimate the peak intensity of the laser pulses is discussed. Section 2.3 explains the HHG chamber where the interaction between intense light and matter occurs. The detail of the dual gas jet apparatus that is the key component of the Gouy phase interferometer is presented in this section. Section 2.4 deals with the detection system of the XUV light pulses generated by the HHG process.

2.1 Table-top ultra-short laser system

The experiments in this dissertation are conducted with a femtosecond laser system. It is a commercial Quantronix Ti:Sapphire based ultrashort laser system which produces 3 mJ, 1 kHz repetition rate, 37 fs pulse, centered at 800 nm wavelength. The pulse duration is further reduced to 9 fs by passing the beam through a Neon filled hollow core fiber followed by the dispersion compensation mirrors. Figure 2.1 shows the schematic of the laser system. It consists of five main sections - the mode locked oscillator, pulse stretcher, two stage multi-pass amplifier, pulse compressor and a hollow-core fibre followed by chirp compensating dielectric mirror pair. The details of each of these components is explained in this section.
Figure 2.1: Optical layout of Quantronix Ti:Sapphire ultrashort laser system along with the hollow core fiber and dispersion compensation mirrors that delivers 9 fs laser pulses.
2.1.1 Mode-locked oscillator

The development of ultrafast pulses was triggered by the invention of laser mode locking. Mode-locking is an interference phenomenon [8, 80] where a large number of longitudinal modes (coherent and phase-locked with each other) in a laser cavity interfere constructively resulting in ultra-short pulse durations in the order of fs. The first section of our laser system is a titanium doped sapphire (Ti:Sapphire) oscillator (model: Quantronix Ti light) with an integrated CW pump laser (model: Quantronix Colibri). The Colibri is a diode pumped compact all solid-state, frequency doubled Nd:YVO4 laser, producing a high quality green beam centered at 532 nm. A Colibri power supply provides the necessary electrical utilities and controls the laser head.

Figure 2.2 depicts the schematic and optical layout of Quantronix Ti-light oscillator. The pump beam is steered into the IR cavity via two plane mirrors placed at 45° to the beam and is focused onto the Ti: Sapphire crystal by a lens. The Ti:Sapphire emission resonates in a folded cavity comprising of two concave mirrors (C1 and C2) and four planar mirrors (M1-M4). The beam of the crystal output is reflected between the output coupler (OC) and the high reflector (HR). One path of the crystal output reflects from C1 and passes through prisms (PR1 and PR2). The spectrally stretched beam reflects off the high reflector and follows the same beam path until it is focused back into the Ti:Sapphire crystal via cavity mirror C1. It is then reflected off the spherical mirror C2 to the OC through the folding mirror M4 (detail explanation is in [81]). A part of the cavity energy is released through the partially transmissive OC. The OC reflects a component of the beam back into the oscillator, following the same path and is amplified with each pass through the Ti:Sapphire crystal.

The oscillator produces ∼ 80 MHz repetition rate infra-red light pulses centred at ∼ 800 nm and the spectral bandwidth is ∼ 35 nm (FWHM). The maximum CW power is ∼ 500 mW. The mode locking is stabilized by translating the C2 mirror from the maximum CW position to a stable mode locking position. The average mode locked output power is ∼ 300 mW. The output spectrum of the oscillator is monitored continuously with an optical spectrometer (model: Ocean optics USB 650).
Figure 2.2: Schematic of optical layout of the Quantronix Ti-light Oscillator. The gain medium is pumped by the Colibri pump laser. The green pump beam is focused into a Ti:Sapphire crystal. Here, C1 and C2 are the first and second cavity mirrors. The output beam of the oscillator is directed into the stretcher. Figure is reproduced from [82].

to determine its spectral bandwidth and whether the laser is operating at the CW or mode-locked condition. The output pulse train is monitored by a photo-diode connected with a oscilloscope. The output light is directed to the stretcher in preparation for amplification. The heat from Ti:Sapphire crystal can be removed by a closed-loop water cooled chiller kept at 20°C temperature.

2.1.2 Odin-II amplifier

The Odin-II amplifier consists of an amplifier and a pump laser integrated into a single box. It is capable of amplifying nJ energy pulse to few mJ by the CPA technique [26,27]. The Odin-II amplifier consists of the following components:

1) Darwin pump laser
2) Pulse stretcher
3) Two stage multi-pass amplifier
4) Pulse compressor
Chapter 2. Experimental set-up and apparatus

Figure 2.3: Optical layout of Darwin-527 series pump laser. Figure is reproduced from [83].

Darwin pump laser

The Darwin-527-50-M is a diode pumped, Q-switched SHG laser that uses Nd:YLF crystal as the laser gain medium to produce horizontally polarized, 1 kHz pulse repetition rate, 527 nm light with an average power of 20 W. The total output power is split into two by a beam-splitter to pump two Ti:Sapphire crystals of the Odin-II amplifier. The first eight pass amplification crystal is pumped with 6 W and the second power amplification crystal is pumped with 12 W power.

The Nd:YLF laser pulse energy is higher compared to Nd:YAG because the upper state life time of Nd:YLF is 480 \( \mu s \), which is considerably longer than that of Nd:YAG upper state lifetime (230 \( \mu s \)). The schematic of the Darwin-527 series is shown in figure 2.3. The Nd:YLF at 1053 nm produces horizontally polarized light. The lens is provided to compensate the natural astigmatism of the Nd:YAG crystal. The acousto-optic modulator and RF driver provides a Q-switch mechanism for the system. An intra-cavity shutter is controlled from the power supply cabinet unit and is included for safety reasons.

Pulse stretcher

Since the output pulse energy from the oscillator is not high enough to utilize in non-linear optical experiments such as high harmonic generation, the pulses needs to be amplified. However, if the fs pulses were amplified straight out of the oscillator, the short pulse duration would give rise to an intensity that would damage the gain
Figure 2.4: Schematics of the stretcher. The output beam from the oscillator is prepared in the stretcher section by temporally stretched it from fs to ps duration in order to inject safely into gain medium of the amplifier. Figure is reproduced from [83].

medium (Ti:Sapphire crystal). To overcome this problem, the output pulse from the oscillator is first temporally stretched by a factor of $10^3 - 10^4$ by introducing a frequency chirp onto the pulse. Figure 2.4 illustrates the optical layout of Odin-II stretcher section.

The seed beam from the oscillator output first passes through a 1:1 beam collimating telescope and then a optical isolator. The Faraday isolator blocks any reflected light re-entering the oscillator. The beam is then incident on the grating center with respect to the upper and lower edge of the grating. The diffracted beam diverges vertically to the spherical mirror which focuses the beam on to the folding mirror. The spherical mirror and folding mirror make a 1:1 telescope. It is reflected off the folding mirror to the spherical mirror and then to the grating with a small horizontal shift to the right. The beam is then diffracted towards the end mirror. The stretcher disperses the pulse and introduces a temporal chirp by introducing a longer path length for the frequencies at the blue end than the frequencies at the red end. The two irises A1 and A2 are for the day to day alignment of the beam from the oscillator output to the amplifier input. This stretched pulse reduces its intensity significantly so it can be safely sent into the gain medium of the amplifier.

**Double stage multi-pass amplification**

Usually the optical gain of the amplifier is limited, so in order to achieve higher gain, the cavity is arranged geometrically in such a way that the light passes through
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Darwin pump laser

Pockel cell

8 pass amplification

2 pass amplification

Ti:sapphire crystal

Ti:sapphire crystal

From stretcher

To compressor

Figure 2.5: Schematic of the double stage Quantronix Odin-II amplifier. Figure is reproduced from [83].

the gain medium multiple times. This is called multi-pass amplification [84] and it involves a number of mirrors to reflect repeatedly with a slightly different path through the crystal amplifier. The Odin-II is a two stage multi-pass amplifier; eight passes for the first stage and two passes for the second stage.

The stretched 80 MHz pulse train is sent into the eight pass amplification section. For the first four passes, the 80 MHz pulse is amplified and then it passes through a Pockels cell. On entering the Pockels cell, the train of pulses will pass through a horizontal polarizer which ensures that all pulses entering the PC are horizontally polarized. When the Pockels cell receives a short high voltage trigger, the polarization of any pulse passing through it at that time will changed to vertical. The Pockels cell selects a single pulse with a repetition rate of 1 kHz from the 80 MHz seed pulse train. This 1 kHz pulses is then sent for another four passes through the same gain medium for further amplification.

The second stage of the amplification is a two pass amplification called the power amplification. Here, the beam passes through a thicker Ti:Sapphire crystal. The crystal is pumped from both sides of the crystal. The power is amplified by four times after this two passes. Figure 2.5 shows the optical layout of the Odin-II multi-pass amplifier.
Figure 2.6: Optical layout of the Odin-II compressor section. Figure is reproduced from [83].

**Grating compressor**

After amplification, the ps pulses are then injected into a double grating compressor in order to compress the pulse duration back to the fs regime by introducing negative group delay dispersion (GDD). The compressor consists of two gratings (parallel to each other) in off-Littrow geometry and a retro-reflector (roof mirror) [83]. Figure 2.6 illustrates the optical layout of the grating compressor. The amplified beam (red line) enters into the compressor through a periscope which reflects it on to the first grating (G1). The diffracted (orange line) beam spread out vertically to second grating (G2). The beam then diffracts off from G2 to the retro-reflector which consists of two rectangular mirrors. The retro-reflector translates the beam horizontally to allow a second pass through the compressor. The second grating G2 is placed on a translation stage that is used to tune the GDD by varying the separation between the gratings. The blue line illustrates the compressed beam exiting the system. More details about this laser system can be found in [81].

Figure 2.7 depicts the pulse characterization after the compressor with a frequency-resolved optical gating (FROG) trace. The measured duration of the output pulse is 37 fs.

### 2.1.3 Hollow core fiber and dispersion compensation mirrors

The final section of the laser system is a hollow core fiber followed by the dispersion compensation mirror (DCM) pair. The optical layout of this section is shown in figure
Chapter 2. Experimental set-up and apparatus

2.8. It compresses 37 fs pulses to 9 fs through an interplay of spectral broadening by self-phase modulation (SPM) [85] in a gas filled hollow fiber and dispersion compensation by negative GDD in the DCM [86]. The spectral bandwidth of the laser pulse out of the compressor is $\sim 30 \text{ nm}$, which is too small to support ultrashort few cycle pulses. The SPM is a non-linear optical effect of light matter interaction that spectrally broadens the bandwidth of the pulse in a gas filled hollow-core fiber. The fiber is a 1 m long fused silica capillary with an inner diameter of 250 $\mu\text{m}$. The fiber is placed on a mount, sitting on v-grooves to keep it fixed in place, and two precise controlled mechanical translators at the input and output edge are used for the alignment. The laser beam is focused into the fiber input by $f=1 \text{ m}$ silver coated spherical mirror. The non-linear optical Kerr effect occurs in gas inside the fiber that lead to a time dependent phase shift. As a result, spectral components are red-shifted at the leading edge and blue-shifted at the trailing edge of the pulse. Neon gas is used as it has a large ionization energy which reduces the chance of multi-photon ionization inside the fiber, a process that is detrimental to the SPM. The gas pressure inside the fiber is kept at differential pumping mode. Differential pumping reduces the
plasma formation at the fiber input. The fiber input is connected with a diaphragm pump so it is kept under vacuum whereas the pressure at fiber exit end is kept at \( \sim 0.2 \) bar above atmosphere. A gas regulator controls the pressure to have optimal spectral broadening.

The output beam from the fiber exit is send to the DCM pair. Figure 2.9 illustrates the working principle of the DCM. It is a dielectric mirror with varying layer thickness so that different frequencies of a broadband spectrum penetrate to different depths into the mirror before being reflected [86,87]. The longer wavelength penetrates deeper into the mirror layer compared to the shorter wavelength. This gives rise to negative GDD. The pulse is compressed to 9 fs duration by means of three reflections on the dielectric DCM pair. A pair of fused silica wedges is used to fine tune the total amount of dispersion, and the insertion of the wedges can be tuned by a translation stage such that the pulse duration is optimized at the point of the experiment.
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Figure 2.9: The working principle of the dielectric multilayer DCM. Multiple layers of variable thickness are deposited on the mirror substrate. The longer wavelength penetrates deeper into the mirror compared to the shorter wavelength before it is being reflected. Figure is adopted from [86].

2.2 Pulse characterization and intensity determination

In order to estimate the peak intensity of the laser pulse, we have to characterize three main parameters: optical power, focal spot size and pulse duration. In this section, we will describe the methods of characterizing these laser parameters.

2.2.1 Optical power

The most fundamental way to observe the performance of the laser is to measure its optical power. A power detector (model: UP19K-15S-W5-D0) is placed onto the laser beam and a power meter (model: Gentec-EO Solo2) provides the signal output and measures the average power, \( P_{avg} \). By dividing the average power with the pulse repetition rate, we can determine the laser pulse energy as \( E = \frac{P_{avg}}{f_{rep}} \), where \( f_{rep} \) is the pulse repetition rate (1 kHz for our laser pulse). Then, the peak power is defined by \( P_p = \frac{E}{\tau_p} \), where \( \tau_p \) is the pulse duration.

2.2.2 Spot size

In order to determine the spot size at the focus, we take the \( 1/e^2 \) beam diameter at different positions of the focus along the laser propagation direction by using a charge-coupled device (CCD) camera beam profiler (model: Thorlabs BC106-VIS).
A beamsplitter (7% reflection) is used to reflect a portion of the infrared laser beam onto the CCD camera. Neutral density filters are placed just before the camera in order to avoid any risk of damage to the CCD. The beam profiler measures the intensity of the beam on a 2D array of pixels and is then fed into an accompanying piece of software. The camera is mounted on a translation stage so that the horizontal (X) and vertical (Y) beam waists at different positions can be measured at both sides of the beam centre. Figure 2.10 depicts the beam diameter at several focal positions along laser propagation direction. The spot size and Rayleigh length can be found by fitting these data with the following equation

\[ w(z) = w_0 \sqrt{1 + \frac{(z - z_0)^2}{z_R^2}}, \]  

where \( w(z) \) is the \( 1/e^2 \) beam waist at a distance \( z \) along laser propagation, \( w_0 \) is the beam waist at the focus, \( z_0 \) is the focus center relative to the translation stage position \( z \) and \( z_R \) is the Rayleigh length.

### 2.2.3 Pulse duration

The pulse duration is measured by using an interferometric autocorrelation (IAC) technique. It characterizes the ultra-short pulses by retrieving the number of electric
field oscillations within full width half maximum (FWHM) of the pulse envelope [88]. Figure 2.11 shows the optical layout of the autocorrelator used for measuring the pulse duration.

The apparatus of the IAC (model: Femtometer F1A) is basically a Michelson interferometer. The input pulse is split into two by a partially coated 1 mm thick beamsplitter (one half on one side and the other half on the other side). This 50:50 coating ensures the same path length and identical dispersion condition for each arm of the interferometer. One arm of the interferometer is fixed while the other one can vary its path length. A variable path length is induced by mounting the retro-reflector of one arm on an electrically driven piezo-electric translation stage which introduces a time delay between the two arms. This delay introduces temporal interference of the two beams. The output beam is focused by a parabolic mirror onto a very thin SHG crystal. A short-pass filter then allows the frequency-doubled light to enter into a photodiode. The path difference between the two pulses (from two arms of the interferometer) causes a time delay $\tau$ that results in a temporal interference at the photodiode. The intensity recorded by the photodiode as a function of the delay is given by

$$I(\tau) \propto \int_{-\infty}^{+\infty} |(E(t) + E(t - \tau))^2|\,dt$$  \hspace{1cm} (2.2)$$

where $E(t)$ is the electric field. The integral is performed over all $t$ as the photodiode response is slow relative to the oscillations of the electric field. A software and electronic component supplied by Femtolasers controls the signal sent to the piezo stage. The number of fringes in the autocorrelation trace is then counted by the software. The software calculates the pulse duration from the measured spectrum from its central wavelength. Figure 2.12 shows the autocorrelation trace and spectrum of the beam measure after the DCM. The measured pulse duration is 9 fs at FWHM and the spectral bandwidth is 90 nm centred at 800 nm.
Figure 2.11: Schematic of the intensity auto-correlator used to measure ultrashort pulse duration. Figure is reproduced from [89].

Figure 2.12: (a) Autocorrelation trace and (b) spectrum of laser pulse. The measured pulse duration is 9 fs at FWHM and a spectral bandwidth is 90 nm centred at 800 nm wavelength.
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2.2.4 Estimate the peak intensity

The peak intensity at the focus of a laser beam is estimated from the measured optical power, focal spot size and pulse duration by the following relationship,

\[ I_p = \frac{2P_p}{\pi w_0^2} P_I, \]  

(2.3)

where \( P_p \) is the optical peak power, \( w_0^2 \) is the \( 1/e^2 \) beam radius at the centre of the focus and \( P_I \) is a constant factor of order unity which depends on the temporal envelope of the pulse. The values of \( P_I \) for the pulses of electric field envelopes shape Gaussian or \( sech^2 \) are 0.94 or 0.88, respectively. Usually, the ultrashort pulses from mode-locked lasers are described to have a \( sech^2 \) shape temporal envelope. However, it is quite difficult to estimate the intensity accurately from the laser parameters by this traditional indirect method so it is not uncommon that peak intensity can be known to a precision of \( \sim 16\% \) even increasing to as high as 50\% [90].

2.3 High harmonic generation section

The intense ultrashort laser beam is focused by a spherical mirror (\( f=750 \text{ mm} \)) into the vacuum chamber where HHG is generated. The generation chamber is a Kimball Physics compact octagon ultra high vacuum (UHV) chamber (model: MCF600-SphOct-F2C8). The chamber consists of eight 2.75" and two 6" conflat (CF) flanges. The apparatus of the Gouy phase interferometer, called the dual gas jet apparatus, is situated inside this chamber. The laser beam enters through a view-port which is mounted on an adapter piece with a 2.75" flange on the cross and exits through the opposite 2.75" flanges that is connected with the HHG detection chamber. The top and bottom gas jet assembly is mounted on the top and bottom 2.75" flanges of the chamber. The gas tubing and electrical connections to operate the pulsed micro valve enters into the chamber through the other two 2.75" flanges via feed-through connectors.

The vacuum pump for the generation chamber is mounted with a 6" flange. It is a turbo-molecular pump (model: Pfeiffer Hi Pace 300) with a pumping speed of
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245 L/s in $N_2$ and rotational speed of 1000 Hz. The backing of the turbo pump is provided by rotary-vane pump (model: Pfeiffer DUO 10 MC). The pressure at the baking stage and generation chamber are determined by a Pirani gauge and an ionization gauge, respectively. The background pressure in the HHG chamber is low $10^{-7}$ Torr, and when gases enter into the chamber during the experiment, the pressure increases up to $10^{-4}$ Torr.

In order to minimize the absorption of generated high harmonic radiation, it is essential to keep the background pressure as low as possible. Thus, a copper gasket having a 1 mm aperture in the middle is attached with the exit CF flange of the generation chamber. This aperture helps to limit the gas flow from the generation chamber to the detection section. Another advantage of using this aperture is only the on axis HHG radiation produced can pass through it and off axis radiations are blocked. In addition, this aperture is used for the initial alignment of the laser to the rest of the experiment. Figure 2.13 represents the images of the high harmonic generation chamber and the subsequent infrared filter wheel chamber. A gate valve separates the HHG detection section from the generation section.

2.3.1 Dual gas jet apparatus

The dual gas jet apparatus is the key component of the Gouy phase interferometer and it consists of two gas jets separated spatially relative to the laser propagation direction. The bottom jet points up and is fixed in position while the top one points down and is movable along the XYZ axes by a triple-axis mechanical translator (model: MDC SPM-1502). First, the laser beam is aligned to the fixed gas jet and then the top jet position is translated to align with the laser beam and the fixed jet. The gas jet is a stainless steel hypodermic syringe (model: Terumo needle: 0.5 mm × 19 mm) that inner diameter is 200 μm. The sharp and plastic ends of the needle are removed by focusing and scanning the laser beam across it. One end of the needle is attached with the needle holder by Torr Seal vacuum epoxy (model: Thorlab TS10). The needle holders and gas jet mounts are custom made mechanical parts built in the Griffith University mechanical workshop. Figure 2.14 depicts the images of individual components of the dual gas jet apparatus.
Figure 2.13: Images of the experimental apparatus. (a) HHG generation chamber. (b) subsequent Al filter section along with gas lines.
Two micro-valves are connected to each gas jet to facilitate switching the gases into the jet according to the measurement protocol. In order to measure relative intrinsic HHG phase difference between two gas species switching the gases in each jet is crucial. A field programmable gate array (FPGA) with LabVIEW graphical programming enables fast switching of the gases in the jets. The pressure in both gas lines is kept at 100 torr measured individually for each gas by capacitance manometer pressure gauges (MKS pressure transducer). A valve located after the leak valve can be used to evacuate the gas jet. Two micro valves are connected with each of the gas jets. Individual gas lines are plumbed via teflon tubing (model: Sigma Aldrich PTFE-58703) to each micro valve from their respective cylinders. The gas cylinder are connected to the other side of the leak valve with more tubing and all connections are made with Swagelok fittings. Both pressure gauges are placed just outside the HHG chamber and the length of gas lines from the pressure gauge to gas jet are kept the same for both jets to ensure the same pressure in both gas jets.

2.3.2 MVC pulsed micro valve

In the advanced Gouy phase interferometer [91], we implemented pulsed micro-valves that actuate electromagnetically and can switch faster than a millisecond. The use of the pulsed micro valve reduces the background pressure in the HHG chamber 6-fold and the synchronization of valve opening with LabVIEW FPGA enables the measurements to be carried out 15 times faster than the prototype version [92].

The micro valves supplied from GYGER Micro Fluidics Solutions (model: SMLD 300 H J 0.15 T1 M F) are operated electromagnetically by solenoid coil (model: SMLD 300 ESP 11Ω L300S). Figure 2.15 illustrates the functional principle of the pulsed micro valve. When no current runs through the coil then the valve is closed. When there is a current feed through the valve coil, the mobile anchor with the valve ball is pulled by the magnetic field off the stationary anchor which opens the micro valve. When micro valve is open, gas enters the chamber as a jet through the needle. In each valve, gases are supplied from the individual gas lines connected to the gas cylinder.
Figure 2.14: Images of different parts of dual gas jet apparatus. (a) Gyger micro valve. (b) needle jet located in mount (top view). (c) needle located in mount (side view). (d) gas jet connected to two micro valves attached with the solenoid coil. (e) Gouy phase interferometer inside the HHG generation chamber. The electrical connections for triggering the micro valves (blue wires) and gas lines (white tubes) are connected into the chamber by feed-through connectors. Figure is adopted from [91].
Figure 2.15: Functional principle of the pulsed micro valve. (a) Micro valve close condition (1. valve nozzle 2. closing spring 3. valve coil/solenoid 4. stationary anchor 5. gas medium 6. valve ball 7. mobile anchor and 8. switch). (b) micro valve open condition [93].

The trigger delay and opening time of the micro valves are synchronized with the 1 kHz repetition rate laser pulses via a FPGA reconfigurable I/O module (model: PCIe-7851) and controlled through a custom written LabVIEW graphical program. The modular valve controller (model: Gyger MVC1) handles the working conditions of the micro valves such as current, duty cycle via java based MVC-software.

2.4 High harmonic detection section

The detection chamber of the HHG radiation is separated from the generation chamber with a gate valve (model: Varian L8500304). This gate valve is opened only when an aluminium (Al) or zirconium (Zr) filter is placed on the detection path to avoid any damage of the spectrometer grating or camera by the IR beam. The detection chamber is pumped by a combination pumping station (model: Pfeiffer Hicube 80Eco) incorporating a turbo pump (pumping speed 67 L/s) and a backing pump. The pressure in the detection chamber is $\sim 10^{-8}$ Torr when the experiment is not running. However, when the experiment is operational the pressure increases up to $10^{-6}$ Torr. The pressure is monitored by a cold cathode compact full range gauge (model: PKR 261) designed to measure pressure range $10^2 - 10^{-9}$ Torr. However, the background pressure and operational pressure in the detection section is not monitored continuously as there is a risk that the gauge can damage the delicate grating of the spectrometer.
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2.4.1 Infrared filter

The fundamental IR and HHG radiation both co-propagate towards the detection chamber. However, the complementary metal oxide semiconductor (CMOS) camera used to image the high harmonics radiation is sensitive to the fundamental 800 nm light so it can easily saturate the camera. Thus, it is necessary to separate the high-powered infrared (IR) pulses from the XUV pulse as it can damage the delicate grating of the spectrometer and the camera. In order to do this, a 200 nm thin Al filter (model: Lebow 0.1Al-0.1Al-L1.0) is placed after the generation stage which appears opaque to the IR but transparent to the XUV light. Figure 2.16 depicts the transmission efficiency of 200 nm Al and Zr filters. This filter has > 60% transmission efficiency from 20-72.6 eV light. In addition, in order to see XUV light beyond 72 eV, a Zr filter is mounted on another ring of the filter holder. The filters are mounted on 10 mm ring into a filter holder which is located in a rotating wheel which allows the filter to be switched during the experiment. However, the experiments presented in this thesis use only the Al filter.

2.4.2 The XUV spectrometer

The XUV spectrometer spectrally resolves the high harmonic generated light. It is a customized commercially available grazing incidence diffraction grating spectrograph (model: Hettrick ES-EUV-K). Figure 2.17 shows the optical layout of the spectrometer.
Figure 2.17: The optical layout of the flat field XUV spectrometer (side view). It consists of a curved mirror and VLS grating. In this diagram, \( \alpha \) is the incident angle of the grating and \( X_{\text{det}} \) is the distance from the grating to the detector, \( y \) is the vertical offset of the diffracted position on the detector. Figure is reproduced from [89].

It consists of a gold coated spherical (concave) mirror and a variable line spacing (VLS) reflective grating. The spherical mirror is curved on the diffraction plane and it focuses the HHG light along the spectrally-dispersed direction. The other direction provides the spatial profile of HHG light. The grating has a variable line spacing and it is custom made for observing the photon energy range suitable for our experiment. The spectrometer allows to disperse the different wavelength in one direction while other direction resolve their spatial profile. The VLS grating offers two advantages compared to a concave type grating; the image plane is flat on the detector and the energy resolution is not dependent on the exact incident angle. The line density of 600 \( mm^{-1} \) allows observation of the spectral regions between 25-90 eV. The spectrometer sits on a base plate with three micrometers to adjust the position and align it to the rest of apparatus of the detection section.

In order to calibrate the spectrometer, we choose two known energy positions of the acquired HHG spectrum; one is the 0\(^{th}\) order position and another is the Al filter cut off energy position that is at \( \sim 72.6 \) eV. Then, by using the diffraction equation

\[
\gamma = \sin^{-1}(m\lambda/d + \sin\alpha),
\]

(2.4)

where \( \alpha \) is the angle of incidence, \( \gamma \) diffraction angle of the grating, \( m \) is the diffraction
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Figure 2.18: Calibration of the spectrometer. Blue and red lines indicate the spectra with Al and Zr filter, respectively. (a) The HHG spectrum in camera pixel axis. The camera pixels positions on the 0\textsuperscript{th} order and Al filter cut-off energy is taken as a reference to calibrate the spectrometer. (b) The spectrum after calibration of the photon energy.

order, $\lambda$ is the wavelength of the light that is diffracted. More information about this particular spectrometer calibration is explained in the thesis [89]. Figure 2.18 presents the calibration of the spectrometer to obtain the XUV energy scale from camera pixel scale.

2.4.3 MCP and camera detector

Figure 2.19 depicts the fundamental apparatus of the HHG detection chamber. The most common type of detector for HHG radiation is the microchannel plate (MCP). It is typically a piece of sliced glass plate with an array of miniature channels where each channel works as an independent electron multiplier [95]. When an XUV photon from HHG radiation is incident on a microchannel of the plate, it frees an electron.
This electron is then accelerated by the applied voltage across the back and front of the MCP which triggers an electron avalanche when it collides with the microchannel walls. The process is repeated multiple times and eventually a gain of $10^7$ electrons is detected at the output for each input photon.

Our HHG detection section consists of a double MCP followed by a very fast P-47 phosphor screen (model: BOS-75-OPT01/DET/P-47) that has $\sim 400$ ns decay time. The imaging area of the MCP is 75 mm and the diameter of each microchannel is $25\mu m$. The maximum electron gain of the MCP is $>10^7$ with an imaging area of 75 mm. We use a macro lens (model: Zoom 7000 Navitar) to image the spectrum with zero distortion on a CMOS camera (model: Basler acA2000-340km). The camera has $2048 \times 1088$ pixels with $5.5\mu m$ pixel size and is cooled with a heat sink to minimize dark current. The voltages across the MCP and phosphor screen are kept at 1.85 kV and 5 kV respectively for a reasonable intensity of the HHG signal. We fixed these voltages for all gas sources to get a comparable signal amplitude and only varied the camera acquisition time in order to obtain a desirable signal level. Figure 2.20 represents the schematic of the overall experimental set-up.
Chapter 2. Experimental set-up and apparatus

Figure 2.20: Experimental layout of all optical components along with high harmonic generation and detection systems. The fundamental IR beam is focused into the HHG generation chamber where the dual gas jet of the interferometer is situated. After the generation chamber, the fundamental IR beam is blocked by an Al filter and the harmonics are propagated into the detection chamber. The spectrometer spectrally disperses the beam, which is then intensified by the MCP image intensifier and finally acquired by a CMOS camera. Figure is adopted from [91].
We have demonstrated an XUV interferometer called “the Gouy phase interferometer” that generates two coherent high harmonic pulses from two independent gas jets placed within a single laser beam focus. This interferometric technique was developed at Griffith University and it has been used to observe the temporal coherence of two XUV pulses from Ar as a target gas with few-cycle laser pulses [92]. The ionization and recombination time (HHG photon emission time) of the electron during the HHG process is determined by the carrier envelope phase (CEP) of the electric field of the driving laser pulse. The Gouy phase shift modulates the CEP of the driving laser within the focus along the propagation direction. Thus, two gas jets of the interferometer placed at different focal positions will experience different electron recombination times. As a result, there will be a delay in photon emission times between the gas jets and this delay induces a phase difference between two HHG pulses. The work presented in this thesis is based on “the advanced Gouy phase interferometer” [91] where a number of improvements have been implemented from the prototype one [92] to make the interferometer suited for future applications, i.e., extracting the intrinsic high harmonic phase shift between the two different gases. The interferometer can deliver unprecedented resolution to impart the delay in electron recombination times between two XUV pulses.

In this chapter, first the working principle of the Gouy phase interferometric technique is discussed. In section 3.2, the temporal coherence of several consecutive harmonic orders with 9 fs and 50 fs driving laser pulses is presented. Section 3.4 discusses the applications of the interferometer. The chapter ends with a discussion on the resolution of our interferometric technique to see how precisely the interferometer
Figure 3.1: Carrier envelope phase of a 9 fs duration (at FWHM) optical pulse. There is a zero offset of cosine shaped carrier wave with respect to the pulse envelope while a $\pi/2$ phase offset for sine shaped carrier wave.

can impart the emission delay between the two XUV pulses.

3.1 Gouy phase interferometer

3.1.1 Gouy phase shift

The electric field of a light pulse is considered as a carrier wave that is contained inside an envelope function. The envelope of the optical pulse propagates with group velocity $v_g$, while the carrier wave propagates with phase velocity $v_p$. The CEP is the phase offset between the carrier wave and the peak of the envelope amplitude. Figure 3.1 illustrates CEP of a pulse of duration 9 fs at FWHM.

The Gouy phase is an axial phase shift originating from the transverse spatial confinement of a focused light beam. When a Gaussian laser beam passes through a focus, the phase velocity increases compared to the group velocity and thus it experiences an additional $\pi$ phase shift with respect to a plane wave within a few Rayleigh lengths as shown in figure 3.2. This geometrical phase anomaly is a general property of any Gaussian beam and was discovered by Gouy in 1890 [96]. The Gouy
Figure 3.2: The propagation of a few cycle pulse through a Gaussian beam. The phase velocity $v_p$ advances compared to the group velocity $v_g$ that converts a “cosine” shape waveform into “-cosine” within few Rayleigh lengths. The experimental points are from [97] where the Gouy phase was observed for a few cycle pulse. The figure is adopted from [37].

Phase shift is defined as

$$\phi_{Gouy} = -\tan^{-1}\left(\frac{z}{z_R}\right)$$  \hspace{1cm} (3.1)

where $z$ is the axial distance from the laser focus along the propagation direction, the Rayleigh length $z_R = \frac{\pi w_0^2}{\lambda}$, where $w_0$ is the $1/e^2$ beam radius at the focus and $\lambda$ is the wavelength.

At the focus of ultrashort laser pulses, the Gouy phase affects the CEP of the driving laser. This phase anomaly for few cycle pulses influenced by the Gouy effect was observed experimentally by Lindner et al. [97]. We built an XUV interferometric technique by utilizing this inherent property of a Gaussian beam. The interferometer can impart a delay between the photon emission time of two HHG pulses with a precision of $\sim 100$ zeptoseconds. Here, we will explain the working principle of this interferometric technique.
3.1.2 Operational principle of the Gouy phase interferometer

The interferometer consists of two spatially separated gas jets located along the propagation direction in a single Gaussian beam focus [91,92]. We know that the ionization and recombination time/phase of an electron during the HHG process depends on the electric field of the driving laser pulse. The Gouy phase modulates the CEP of the laser pulse and so it changes the electric field at different locations within the focus. Thus, the trajectory that the ionized electron takes is different for the two gas jets placed at different locations and subsequently it introduces a delay $\Delta t$ in the HHG photon emission time. This delay manifests itself as a phase difference, $\Delta \phi$ between the two XUV pulses generated from the top and bottom gas jets of the interferometer. Figure 3.3 depicts the schematic and basic principle of the Gouy phase interferometer.

A first order semi-classical model on the free electron trajectory is introduced to explain and understand the mechanism of HHG phase shift observed from the Gouy phase interferometric technique [92]. From the Lewenstein model [58,59], the emission phase of a particular harmonic order $q$ is given by

$$\phi = q\omega t_r - \frac{1}{\hbar}S(p_{st}, t_i, t_r),$$

(3.2)

where $\omega$ is the angular frequency of the laser pulse, $S$ is the semi-classical action in momentum space, which depends on the canonical momentum $p_{st}$, the electron ionization time $t_i$, and the recombination time $t_r$. This semi-classical action term is actually the quantum phase of the recombining electron and it describes the free electron motion in the laser laser field. The first term of equation 3.2 is related to the electron recombination time which is shifted with the Gouy phase and modified at a position $z$ away from the focus ($z = 0$) by the relationship [92],

$$t_r(z) = t_r(z = 0) + \frac{\phi_{\text{Gouy}}(z)}{\omega},$$

(3.3)

where $t_r(z = 0)$ is the electron return time where the Gouy phase has no influence and it happens exactly at the center of the laser focus. The equation 3.3 is reasonable...
when the intensity of the laser beam at both gas jets position is almost the same, otherwise significant intensity variation may alter the electron trajectories required for a particular harmonic order. The intensity of a Gaussian beam varies away from the focus as

\[ I(z) = \frac{I_0}{1 + (z/z_R)^2}, \] (3.4)

where \( I_0 \) is the peak intensity at \( (z = 0) \). Our measurement is limited to the gas jets separation within region where intensity variation is small.

The semi-classical action term of equation 3.2 depends on the laser intensity and the electron travel time \( \tau_e = t_r - t_i \), i.e., \( S \propto I \times \tau_e \). Therefore, the total phase difference of the \( q^{th} \) harmonic order generating from two gas jets sitting at \( z_1 \) and \( z_2 \) positions in figure 3.3 is [92]

\[ \Delta \phi \approx q(\phi_{\text{Gouy}}(z_1) - \phi_{\text{Gouy}}(z_2)) + q\omega(\tau_e(z_1) - \tau_e(z_2)) - \frac{1}{\hbar}(S_1 - S_2). \] (3.5)

Combining electron travel time and semi-classical action terms into \( \phi_{\tau,S} \) and approximated the equation 3.5 by first order Taylor series expansion, we get [92]

\[ \Delta \phi \approx q\frac{d\phi_{\text{Gouy}}}{dz}\Delta z - \frac{d\phi_{\tau,S}}{dz}\Delta z. \] (3.6)

Within the focus, where intensity of the laser beam varies slowly, the second term of this equation will be close to zero. Equation 3.6 implies that a small shift of Gouy phase results in a phase shift between the two XUV emissions that is \( q \) times larger. The phase shift leads to a constructive to destructive interference between the two XUV pulses depending on the separation, \( \Delta z \) between the gas jets.

### 3.2 Temporal coherence of consecutive harmonics

Before observing the temporal coherence of the high harmonic pulses, we optimized the HHG signal at varying target gas pressure and trigger delay between the laser pulse and micro valve opening. Pulsed gas valves are used in the advanced Gouy phase interferometer [91] rather than a continuous jet as it reduces the background pressure in the HHG generation and detection chamber by \( \sim 6 \) fold. The description of the dual gas jets apparatus for the advanced Gouy phase interferometer is given
Figure 3.3: The principle of operation of the Gouy phase interferometer. (a) A Gaussian IR laser beam is focused and two jets are placed face to face within the focus. The gas jets are separated in space along the laser propagation direction. The HHG radiations are generated from both gas jets by a single laser pulse. The phase of the HHG pulses depends on the associated gas jets position. (b) Gouy phase shift at different positions within the laser focus along the propagation direction for Rayleigh length, \( z_R = 14 \) mm. Due to the Gouy phase shift, the CEP of driving laser field changes that turns into a \( \pi \) phase shift over a Rayleigh length (\( \pm z_R \)). (c) The CEP of the driving laser experienced by the gas jets at \( z_1 \) and \( z_2 \) positions is different. As a result, a delay \( \Delta t \) is introduced in harmonic photon emission time and thus a phase shift, \( \Delta \phi \) between the two XUV pulses. Figure is adopted from [91].
in chapter 2. After optimization, we kept the gas pressure in both jets at 100 Torr and the trigger delay between laser pulse and micro valve opening at 700 µs for the rest of the experiment. For a pressure > 100 Torr, the phase matching condition is still good, but it increases the background pressure in the HHG detection chamber to $> 2 \times 10^{-6}$ Torr, which is detrimental to the MCP detector.

We optimized the laser beam position on the top and bottom gas jet tips. While optimizing, the HHG signal on the CMOS camera is monitored as a feedback to get the maximum yield. The vertical and horizontal positions of the beam with respect to the optical table is aligned by the steering mirror sitting before the HHG generation chamber in order to place it on the tip of the bottom gas jet (fixed in position). Next, the longitudinal position of the beam is adjusted on the bottom jet tip to place it at the focus. After that, the top jet is placed before the focus and its position is adjusted to align it with the laser beam and the bottom jets by the three axes mechanical translator.

The temporal coherence properties of high harmonic radiation is observed for a range of harmonic orders with atomic Ar and molecular $H_{2}$ target gas. The experiment is conducted with 9 fs and 50 fs laser pulses. The CEP of the laser pulse is not locked (random CEP) for all the experiments presented in this thesis.

### 3.2.1 With 9 fs driving laser pulses

*Ar gas as a HHG source*

Argon ($Ar$) is used as the first target gas to test the advanced Gouy phase interferometer. The temporal coherence of the high harmonics are observed at various gas jet separations with Ar gas in both jets. Figure 3.4 presents the normalized intensity for a range of harmonic orders from H23 to H35 by varying the gas jet separation from 0 mm to 7.6 mm with a step size of 0.315 mm. The separation between the jets is varied by moving the top jet away from the bottom jet along the laser propagation direction. For each separation, HHG spectra with individual gas jet ON, and both gas jets ON are acquired. Then, the intensity with both jets ON is normalized by
the coherent sum of intensities from either jet ON by

\[ I_N = \frac{I_{BT}}{I_B + I_T + 2\sqrt{I_B I_T}}. \]  \hspace{1cm} (3.7)

where \( I_B, I_T \) and \( I_{BT} \) are the HHG yields with bottom, top and both gas jet ON, respectively. Here, \( I_{BT} \) is the coherent sum of two XUV pulses providing a phase difference \( \Delta \phi = q\Delta \phi_{Gouy} \) (if only caused by the Gouy phase shift) between them and expressed as

\[ I_{BT} = I_B + I_T + 2\sqrt{I_B I_T} \cos(q\Delta \phi_{Gouy}). \]  \hspace{1cm} (3.8)

When the separation between the jets is zero, HHG emissions generated from the two gas jets interfere constructively. As the separation increases the HHG radiation emitted by the movable jet (top jet) undergoes a phase shift in respect to the fixed one (bottom). It is observed clearly that each harmonic exhibits constructive and destructive interference as the separation between the jets is varied and the periodicity of the fringes decreases with increasing the harmonic order. For example, H27 harmonic experiences the first coherent revival (2\( \pi \) phase shift) at \( \Delta z = 6.5 \) mm while for H33 the same amount of phase shift occurred at \( \Delta z = 4 \) mm. The observed fringes are mainly due to the Gouy phase shift of the IR laser beam that imparted a HHG emission delay between the two pulses generated from top and bottom gas jets. However, the normalized intensity at its revival distance does not reach to the original value as it is for overlapping jets position. This may be due to a small focal volume change and laser intensity difference between the two jets placed at different locations within the focus.

**Retrieval of Rayleigh length**

For further analysis and to test the original assumption about the phase shift between the two XUV pulses explained by first order semi-classical model in section 3.1, we retrieved the Rayleigh length from the coherence data. We plot the HHG yield for individual harmonic order with gas jet separation. These data points are fitted with
a decaying cosine function as shown in figure 3.4(b) and the fitted function is

\[ I_N = ae^{-bz}\cos(cz) + d \]  

(3.9)

where \( a, b, c \) and \( d \) are the fitting parameters. From this fitting, we get the separation where \( 2\pi \) phase shift occurs and this separation is called the first coherent revival distance, \( z_c \). Then, by rewriting equation 3.6 with the conditions, \( \Delta \phi = 2\pi \) and \( \Delta z = z_c \) as [92]

\[ \frac{1}{z_c} = \frac{1}{2\pi} \left[ q \frac{d\phi_{Gouy}}{dz} + \frac{d\phi_{r,S}}{dz} \right] \]  

(3.10)

Figure 3.5 shows the inverse coherent revival distance, \( \frac{1}{z_c} \) vs harmonic order, \( q \). From a linear fitting of these data points, we can get the first and second derivative terms of equation 3.10. The red line is the fit to data using the Gouy phase derivative \( \frac{d\phi_{Gouy}}{dz} \) and semiclassical action derivative \( \frac{d\phi_{r,S}}{dz} \) as the fit parameters. The blue solid line indicates the theoretical prediction when only the Gouy phase is considered and it is calculated with the Rayleigh length of the laser beam measured from the beam profile.

The retrieved Rayleigh length of the driving laser pulse from the fitted curve with the experimental data points is 15.48±2.06 mm (using the small angle approximation \( \tan(\theta) \approx \theta \)). The estimated Rayleigh length from the beam profile is 14.95±1.5 mm. This agreement with the Rayleigh length measurement and the retrieved Rayleigh length supports the conclusion that the phase shift between two XUV emissions occurs mainly due to the Gouy phase variation of the driving laser. The action derivative term estimated from the y intercept of the fitted line is \(-101±34.1 \text{ rad/m}\). Theoretically this term is assumed to be zero near the laser focus where intensity is varied slowly.

**H\textsubscript{2} gas as a HHG source**

We tested the coherence properties of the high harmonic with molecular hydrogen(H\textsubscript{2}) target gas. In general, the ionization and recombination processes of HHG in molecules are much more interesting and complex than atomic systems due to the
Figure 3.4: Temporal coherence of the consecutive higher order harmonics generated from $Ar$ gas with a 9 fs, 800 nm pulse. (a) Normalized HHG yield from H23 to H37 by varying the gas jets separation from 0 to 7.6 mm. The harmonics are interfered constructively and destructively depending on the relative separation between the gas jets along Gaussian beam focus. Higher the harmonic order faster the phase shift upon separation. (b) The degree of coherence for H27 at varying gas jet separations and the fitted curve. (c) A reference HHG spectrum from $Ar$. 
Figure 3.5: The inverse of the coherent revival distance with Ar gas from H23 to H33. The red solid line is the fitted line to the experimental data obtained from figure 3.4 where the derivative of the Gouy phase and semiclassical action phases are presented. The blue solid line represents theoretical prediction when only Gouy phase is considered.

additional degrees of freedom in their nuclear motion. Additionally, compared to Ar obtaining a high-yield HHG signal from H2 is very challenging. The reason is the compression ratio of a turbo molecular pump decreases exponentially with molecular weight [98]. In comparison to Ar, the compression ratio of the lightest H2 molecule decreases by $\approx 130$ times, so it is harder to pump [99]. In particular, to avoid any unexpected damage of the MCP image intensifier, it is important to maintain the background pressure to less than $2 \times 10^{-6}$ Torr. However, with the implementation of pulsed micro-valves and synchronization of the valve opening time with laser pulses, we are able to increase gas density in the interaction region while keeping the background pressure low, which enables us to get a sufficiently strong HHG signal from H2 gas.

The normalized HHG signal with H2 as the target gas from harmonic order H23 to H37 is depicted in figure 3.6. The fringe visibility at the higher order harmonics is better for H2 than for Ar. There is a prominent minimum in the HHG spectrum in Ar called the Copper minimum at an energy about 53 eV ($\sim H35$) [100] that leads to lower harmonic yield around this energy. The retrieved Rayleigh length of the driving laser from the fitted line of figure 3.7 is $16.7 \pm 1.6$ mm. The action derivative
3.2.2 With 50 fs driving laser pulses

In the case of multicycle laser pulses, high harmonics are generated from many optical cycles with slight intensity differences between each cycle. The spectral width of each harmonic order is narrower and the peaks are sharper compared to the harmonics generated from few-cycle pulses. A theoretical work on the Gouy phase interferometer showed that the extracted Rayleigh length from the harmonic coherence observation is more accurate for longer driving laser pulses than shorter pulses [101]. This is because the narrower peaks from the longer pulse duration allow the coherence revival position to be determined with greater accuracy. Here, we tested experimentally the coherence properties of the XUV pulses with multicycle laser pulses. The pulse duration measured with a FROG trace is 50 fs.
Figure 3.7: Inverse coherent revival distance as a function of harmonic order from $H_2$ gas with 9 fs pulse. The red solid line is a curve fit to the experimental data where the derivative of the Gouy phase and semiclassical action phases are presented as explained in equation 3.10 and the blue solid line represents the inverse revival distance when only the Gouy phase contribution is considered.

The temporal coherence of 8 consecutive harmonic orders by varying the jet separation from 0 mm to 6 mm with $H_2$ as the HHG generation medium is shown in figure 3.8. The fringe periodicity increases linearly with increasing the harmonic order. We observed very distinct 1$^{st}$ coherence revival peaks and even 2$^{nd}$ coherence revival peaks for higher order harmonics. The periodicity of fringes with 50 fs laser pulses is shorter compared to the result that we have observed from 9 fs pulses. This is due to the different Rayleigh length of the laser beam. The driving laser beam of 50 fs pulses has some astigmatism and the spatial profile is not symmetric (beam parameters for x and y direction are not similar). However, the main hypothesis of the Gouy phase interferometric technique is still working well. The average Rayleigh length of the laser beam measured from beam profile is $8 \pm 1.5$ mm. The retrieved Rayleigh length from the 1$^{st}$ coherent revival distance (figure 3.9) is $10.76 \pm 1.12$ mm and action derivative term $-73.45 \pm 42.35 \text{ rad/m}$.

In order to get a few cycle laser pulse, additional experimental equipments such as hollow core fibre for spectral broadening and subsequent dispersion compensation optics are necessary that would make the experiment expensive. Moreover, not all HHG experimental laboratories have few cycle laser pulse facility. The above observation of the temporal coherence using the Gouy phase interferometric technique
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Figure 3.8: Temporal coherence of high harmonics with 50 fs laser pulse with $H_2$ target gas. (a) Normalized yield of 8 consecutive harmonic orders as a function of gas jets separation with 50 fs driving laser pulses. (b) HHG yield for $H_2$ at varying gas jets separation and the fitted curve. (c) a reference HHG spectrum.

confirms that our technique can be used to perform the HHG experiment with multi-cycle laser pulses. This measurement is an indication of broader usefulness of Gouy phase interferometer.

3.3 Spatial coherence of the two XUV pulses

We observed the spatial profile of the XUV beams to see the difference of divergence angle between the emissions from two gas jets. Figure 3.10 depicts the spatial profile of 25th harmonic order when the gas jets are placed at a separation where the 1st coherent revival occurs for this harmonic order. The distance between the HHG interaction region and detector is $\sim 1$ m. The red line shows the beam profile with both gas jets ON and blue line is only with top jet ON. There is no significant diffraction observed between the two curves, so we can conclude that the emissions
3.4 Applications of the Gouy phase interferometer

High harmonic generation is a potential source of table-top coherent XUV and soft X-ray light pulses with attosecond duration. This coherent laser-like short wavelength pulse generation technique continues to develop but there are three major challenges that still restrict it for future experimentation in order to achieve the goal of HHG spectroscopy. These challenges are: extension of harmonic cut-off energy, conversion efficiency enhancement and controlling the HHG spectral shape by enhancing signal for single or several selected harmonic orders [41]. By using successive gas jets, the Gouy phase interferometric technique can enhance the HHG yield and select a particular or range of harmonics with high contrast ratio compared to the adjacent ones.

3.4.1 Increased HHG yield

The possibility of using coherent light generated from the HHG process for further applications depends on the brightness of the sources. Thus, maximizing the HHG yield is a major goal to utilize the coherent XUV light for future applications such as ultrafast coherent imaging of atoms and molecules, implementing nonlinear
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Figure 3.10: Observing the far field spatial profile of the 25\textsuperscript{th} harmonic order. The red lines shows the profile with both gas jets on and blue line is only with top jet ON.

phenomena in the XUV range, or using it as a seed pulse of soft X-ray lasers [102,103]. The low photon flux of HHG partly comes from phase mismatching in the nonlinear medium and partly from the weak response of the individual atoms/molecules to the laser field. There are several approaches that can be taken in order to increase HHG photon flux [62,104–107]. Brizuela et al. have improved the photon flux from a Ne gas cell by adding another Ar filled cell before Ne [107], and Pirri et al. improved the HHG quasi phase matching condition by using arrays of gas jet sources that increase the coherence length [62].

The Gouy phase interferometer demonstrates improved HHG yield over the whole observable spectral region. When the separation between the gas jets is zero and if HHG pulses are generated from both jets with the same gas, their irradiance will be added together (constructively interfering with each other, assuming no phase difference). Ideally the resultant yield will be 4 times compared to the yield with a single gas jet (see equation 3.7). Figure 3.11 shows the experimental results on comparison of HHG yield from single and dual gas jets. The experiment has been
conducted separately with two different gases, Ar and $H_2$. It is observed that HHG yield can be increased by more than three times with both jets compared to the single jet.

### 3.4.2 Selective control of HHG spectral shape

**Short pulse**

The typical HHG spectrum is a frequency comb with nearly equal intensity of the harmonics in the plateau region. However, selection of single harmonic from this harmonic comb is important to utilize it as a monochromatic coherent source. The monochromatic harmonic is also useful for applications such as seeding of an XUV free electron laser to get a fully coherent output [103].

![Figure 3.11: The comparison of HHG yield from single and dual gas jet with (a) Ar and (b) $H_2$ as a generating medium. The signal is increased by more than 3 times with dual gas jets compared to a single jet.](image)
of harmonic spectra are also interesting for applications such as stationary or
time-resolved spectroscopy in the XUV and soft-x-ray regions [108]. Some previous
experimentation could able to shape the high harmonic spectra to a range of spectral
energy by adaptive control schemes to tailor the driving laser pulse prior to the HHG
generation [41,109–111]. The adaptive control schemes relies on an evolutionary
algorithm that selects optimal electric fields. Other groups achieved selective control
of single harmonics by controlling the phase of multicolor driving laser fields [112].
However, the control of a specific harmonic or a range of harmonic orders with
increased yield with the gas jet geometry and linearly polarized light was considered
to be impossible [41].

The Gouy phase interferometric technique can be used to shape the spectral
properties to select a particular or a range of harmonics with increased yield. The
spectral shape is controlled by simply varying the separation between the gas jets
along the laser propagation. This technique does not require any driving laser
pulse shaping with a complicated adaptive control mechanism, an evolutionary
computer algorithm [41,109], nor does it need to include any additional optics or
instrumentation. By using successive gas jets within the Rayleigh length of a single
laser focus, we can increase the HHG signal for a range of harmonics simply by
tuning the separation between the jets. We know that the phase shift of XUV pulses
is $q$ times the Gouy phase shift of the driving laser. Therefore, for a particular gas
jet separation the phase shift of the XUV pulses is different for each of the harmonic
order, and thus, some of harmonics will interfere constructively, while others will
interfere destructively.

Figure 3.12 depicts the HHG spectrum from $H_2$ at six different gas jet separations.
The signal at $\Delta z = 0$ mm is a reference spectrum of $H_2$. At separation $\Delta z = 2.53$
mm, the signal from lower order harmonics is suppressed while higher orders are
increased. At a larger separation $\Delta z = 4.75$ mm, lower order harmonics have stronger
signals while higher harmonics are suppressed. At $\Delta z = 7.6$ mm all the harmonics
other than H23 is suppressed.
Figure 3.12: Selective control of HHG spectrum with a 9 fs, 800 nm pulse from $H_2$ at different separation between the gas jets. Both, the enhancement and the suppression of a single or a range of harmonic orders can be achieved by tuning the gas jet separation. Each individual graph is normalized to its maximum value.
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Figure 3.13: Optimization of harmonic spectral shape with a 50 fs driving laser pulse. The separation between the gas jets is varied to select a single harmonic or a range of harmonics with a higher yield with respect to the adjacent ones.

**With multi-cycle laser pulses**

The Rayleigh length of our laser beam for multi-cycle pulse is shorter than that of the 9 fs pulse. Figure 3.13 shows the HHG spectrum with 50 fs laser pulse at different gas jet separations. It is shown that we can optimized two consecutive harmonic orders at higher yield by altering the gas jets separation. We believe that it is possible to optimize the HHG spectrum for a single harmonic order by adjusting the Rayleigh length of the driving laser.

### 3.4.3 Extracting the relative HHG phase between two gases

The most prominent application of the Gouy phase interferometer is its ability to extract the relative intrinsic phase shift between two HHG generating atoms or molecules. The full mapping of the harmonic dipole is crucial for molecular orbital
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tomography. The phase is particularly important to map the harmonic dipole phase completely for molecular orbital tomography [113] but difficult to extract for XUV pulses because of its very short wavelength. The interferometer can extract the phase of two atom/molecules if the ordering of the gases in the two jets is altered. We will discuss in detail about the phase extraction procedure and present the results from hydrogen and methane molecular isotopes in the next two chapters of this thesis.

3.5 Temporal resolution of the interferometer

The phase shift between the two XUV pulses that we have observed so far actually comes from the photon emission time delay between the two jets and this delay depends on the gas jet separation. Here, we estimate how precisely the Gouy phase interferometer can resolve this emission time delay between the two XUV pulses. By measuring the fluctuations of intensity, an estimation about the time resolution of the interferometer can be calculated. This can be understood from equation 3.7 that illustrates how the HHG intensity is varied with phase shift.

The procedure of obtaining the temporal resolution is as follows: by placing the gas jets at the separation where both jets have similar HHG yield, $I_{BT}$ with both gas jets ON is acquired continuously in 100 ms time interval. This intensity is then normalized by acquiring the HHG signal from individual gas jets ON. The normalised intensity caused by the Gouy phase shift is given by

$$I_N \approx 0.5 \cos(q\Delta \phi_{\text{Gouy}}) + 0.5$$

Thus, from the intensity data, the Gouy phase shift can be obtained. The phase shift is then converted to emission time delay as

$$\Delta t_r = \frac{\Delta \phi_{\text{Gouy}}}{\omega},$$

where $\omega$ is the angular frequency of the driving laser. We have estimated the resolution of the interferometer through a measurement of Allan deviation. The Allan deviation characterizes the uncertainty of a measured quantity as a function of
Figure 3.14: Allan deviation of 25th harmonic order for estimating the temporal resolution of the Gouy phase interferometer. The ultimate resolution is $\sim$ 130 zeptoseconds at 23 sec and it is $<200$ zeptoseconds for an averaging time between 9 sec and 85 sec.

the experimental measurement time. By monitoring this dependence, the optimum measurement time can be chosen. The overlapping Allan deviation method is used for the estimation and it is defined as

$$\sigma_{\text{Allan}}(\tau) = \left( \frac{1}{2(N - 2m)} \sum_{i=1}^{N-2m} (y_{i+m} - y_i)^2 \right)^{1/2}, \quad (3.13)$$

where $\tau$ is the averaging time, $N$ is the total number of samples and $m$ is the averaging factor, $y_i$ is the $i^{th}$ sample of emission time delay in time series. Figure 3.14 shows the calculated the Allan deviation of timing resolution as a function of measurement time. The best resolution is $\sim$ 130 zeptoseconds at 23 sec measurement time and it is $<200$ zeptoseconds for an averaging time between 9 sec and 85 sec.

The Gouy phase interferometer is a passively stabilized interferometer as no active stabilization act is involved. The high resolution of this interferometer comes from the fact that any vibration of the apparatus (gas jets) is compared with the Rayleigh length of the driving laser focus, while in the traditional interferometer it is compared with the wavelength of the radiation.
3.6 Summary

The working principle of the Gouy phase interferometer has been discussed. Then the temporal coherence of the XUV photons generated from dual gas jets of the interferometer from Ar and H$_2$ gases is presented. The experiment is conducted with 9 fs and 50 fs driving laser pulses. It has been shown that the interferometer works well for both laser pulses. Producing few cycle laser pulses is difficult as extra experimental components for spectral broadening (with a hollow core fibre) and introduction of negative GDD (by chirp compensation mirrors) need to be added, making the experiment more complicated. This demonstration of coherence properties proves that the interferometer is able to work well even with multi-cycle laser pulses. We also described a few promising applications of this interferometric technique including enhancing the HHG yield, controlling HHG spectral shape to select a particular or a range of harmonics at higher intensity compared the neighbouring ones and extracting the relative phase of HHG emissions from two gas species. Finally, the chapter concluded with an estimation of the timing resolution of the interferometer.
Relative phase and attosecond emission delays for HHG from molecular hydrogen isotopes

High harmonics spectroscopy (HHS) has offered great opportunities to image the molecular structure and dynamics with attosecond temporal resolution and angstrom spatial resolution as discussed in the introduction chapter. The HHG process results from light-matter interaction which occurs within half of a driving laser optical cycle. During this interaction, all the parameters such as free electron dynamics and how it is influenced by the Coulomb potential, nuclear dynamics, bound electrons in the ion and their interactions with ionized electron are imprinted on the amplitude and phase of the emitted HHG radiation. However, all the information is encoded into one spectrum (and phase) and decoding the signal to disentangle and understand the contributions from different factors and processes is a very challenging task. The desired information is encoded in both the amplitude and phase of the high harmonic emission and HHS strives to measure both. Although the phase of HHG is important for tomographic imaging of molecular orbital wavefunctions, the sensitivity of optical detectors only for intensity limits the number of experimental works on HHG phase measurements. So far there has been a good number of experiments performed to observe the molecular structural information by measuring the HHG spectral intensities [66, 67, 70, 73] but very few on the HHG phase measurement [114, 115].

Interferometry is the most common and natural approach for measuring the phase of electromagnetic fields. Typical interferometric techniques such as Michelson, Mach-Zehnder or Sagnac interferometers split the beam into two paths and a delay is introduced into one arm with respect to another. Then the two beams are recombined
Chapter 4. Relative phase and attosecond emission delays for HHG from molecular hydrogen isotopes

(made to interfere) and the amplitude of the combined field is measured to extract the relative phase information. However, building an interferometer in the XUV region is not as simple as in the visible or infra-red range. This is due to the low refractive index of materials for XUV light, making optics for those wavelengths expensive and delicate, if at all available. In addition to that, controlling the delay between two replicas of the field with subcycle stability required for interferometric measurements is difficult because of the extremely short wavelength (oscillation period) of XUV light. The path length stability needs to be on the nanometre scale, which is difficult to maintain in a lab environment.

To overcome those difficulties, we designed and built ‘the advanced Gouy phase interferometer’ in order to extract the relative phase shift of high harmonic radiation between two different gases. This technique is an all optical method and an elegant way to generate two coherent HHG pulses without any necessity of splitting the driving laser or high harmonic beam. The two mutually coherent XUV pulses are generated by exploiting the inherent properties (Gouy phase) of a focused Gaussian beam. This technique is able to generate two XUV pulses with emission delays within the half-cycle of the driving laser optical pulse and to measure those delays with a precision of $\sim 100$ zeptoseconds.

This chapter describes how we measured the relative phase shift between HHG pulses generated from hydrogen molecular isotopes using 9 fs and 50 fs driving laser pulses. The section 4.1 provides a brief review of the existing XUV interferometric techniques for observing the coherence properties as well as the phase shift measurement of HHG radiation from different atoms and molecules. Section 4.3 describes the motivation behind choosing the hydrogen isotopes as the first target to measure the HHG phase shift. The derivation of relative phase shift from $H_2$ and $D_2$ by using the Gouy phase interferometric technique is explained in section 4.4. The experimental setup, measurement protocol, data acquisition and analysis are described in section 4.5. The following section presents the experimental results and discusses their interpretation on the basis of theoretical modelling. Then, the chapter is concluded with the summary.
Chapter 4. Relative phase and attosecond emission delays for HHG from molecular hydrogen isotopes

4.1 XUV interferometry: An overview

There is a number of interferometric techniques developed to observe the phase in XUV domain from high harmonic emission [114,116–124]. The Reconstruction of Attosecond Beating By Interference of Two-photon Transitions (RABBITT) is a successful way for temporal characterization of attosecond pulses and pulse trains [34,115,125]. It measures the relative phase between neighbouring harmonic orders from two color (XUV+IR) photoelectron spectrum at varying delays between the XUV and fundamental IR field.

Another technique is called the two-source interferometry (TSI) which can be implemented in different ways. One of them is splitting the driving laser pulse into two and focusing them at different locations on a single gas jet separated spatially (in the direction perpendicular to the laser propagation). It is an all optical technique where two coherent harmonics are generated from single gas jet and a spatial fringe pattern is observed when the two XUV beams interfere at the far field [116, 117, 120, 126]. That scheme is very similar to Young’s double slit experiment resulting in a fringe pattern. This type of interferometer technique is used to characterize the intrinsic and dipole phase of HHG emission. However, this technique suffered from the required nanometer scale stability that restricts its practicality and wider adoption in the community [116]. Recently, a TSI method measured the absolute phase difference between two noble gases with two individual gas jets [124]. Another interferometric technique for measuring the relative phase involves using a mixture of two gases in a single gas jet. In this method, the HHG amplitude measured for the mixed gas is compared with corresponding amplitudes for each of the gases. This technique has been used to observe the electronic and nuclear dynamics of atoms and molecules from harmonic phase [114, 122, 123, 127]. Usually a mixture of an atomic and a molecular gas with similar ionization potential is used and the atomic target is used as a reference. However, the measured spectral intensity gives access to the cosine function of the relative phase so the sign of the phase (and corresponding emission delay) is ambiguous in this case [123,127].
Chapter 4. Relative phase and attosecond emission delays for HHG from molecular hydrogen isotopes

We developed a promising new XUV interferometric technique that can effectively measure the relative phase shift from two different gas species with an unprecedented resolution. The two gas jets with different species are separated spatially (along the laser propagation direction) in a single laser focus. The method utilizes the inherent properties of the driving IR focused beam to generate two mutually coherent XUV pulses. The HHG pulses are generated from both jets by a single laser pulse but with a phase difference between them due to the Gouy phase of the driving laser (the principle of operation and the experimental apparatus have already been explained in detail in chapter 3).

4.2 HHG in molecules

Compared to atoms, the physical picture of the HHG three step model is different and much more complex in case of a molecular target, as the additional nuclear vibrational and rotational degrees of freedom play an important role. The typical rotational and vibrational motion of nuclei occur on ps and fs time scales, respectively, while electron movement happens on the as timescale. In addition, molecules have much complicated electronic structure compared to atoms.

When a strong laser field ionizes a molecule, it launches a free electron wavepacket in the continuum along with correlated bound state electron and nuclear wavepackets. The free electron wavepacket accelerates away from the parent ion in the continuum driven by the laser field and at the same time the ground state nuclear wavepackets evolve over time with nuclear wavepacket moving on the potential energy surface as shown in figure 4.1 for $H_2^+$. Finally, after the driving electric field reverses its direction following a certain time delay the electron returns back to the parent ion and recollides with it. In the recollision process, the continuum and bound wavefunctions interfere and induce an oscillating dipole [40]. This oscillating dipole emits high harmonic radiation on which the amplitude and phase of the molecular dipole is imprinted. Thus, the emitted photons carry dynamical and structural information about the molecules during the ionization and recombination events. In molecules, laser driven nuclear motion can modulate the harmonic intensity and phase.
4.3 Motivation for selecting the hydrogen isotopes

After the first discovery in 1913 [128], isotopes have attracted great attention due to their applications in every field of science. The isotopes have different nuclear masses and thus different vibrational and rotational frequencies. Hydrogen ($H_2$) is the simplest molecule in nature and deuterium ($D_2$) is its only stable isotope. The reason behind choosing hydrogen as the first target species for phase shift measurement in this thesis is that it is the simplest neutral molecule having only two electrons and two nuclei. The non-rotational nuclear motion occurs along the single coordinate -
the inter-nuclear axis. Moreover, the hydrogen nuclear dynamics is the fastest of all diatomic molecules because protons and deuterons are the lightest nuclei. At the same time their mass ratio is the highest of all isotopes, with the \( D_2 \) molecular mass being twice than that of \( H_2 \) so the isotopic effect can be the strongest compared to other molecular isotopes. The comparative structural information of \( H_2 \) and \( D_2 \) is shown in table 4.1. The hydrogen molecule has two protons and no neutron while deuterium has two protons and two neutrons. Both of them have two electrons and linear inter-nuclear separation with only one H-H / D-D covalent bond. These isotopes are relatively abundant and affordable in price. In addition to that, detailed theoretical analysis with as few approximations as possible is also necessary to understand and validate the experimental results. The hydrogen molecule, with only two electrons and two nuclei, is easier to compute quantum mechanically (including the electron-electron interactions) than any other neutral molecule. In fact, it is the only molecule for which \( \text{ab initio} \) modelling with minimum amount of approximations is currently possible. Thus, it can serve as a benchmark molecule for any experiment and modelling and as a useful reference or model for future experiments with more complex target molecules.

By comparing the high harmonic intensity and phase from hydrogen isotopes, the effects of nuclear vibrational motion have been predicted theoretically [130]. Later that prediction was verified experimentally by observing the amplitude modulation (AM) of the HHG spectrum [66, 67, 73]. It was shown that the HHG yield for heavier \( (D_2) \) isotope is higher than the lighter \( (H_2) \) isotope and that is due to the slower nuclear vibrational motion of \( D_2 \) compared to \( H_2 \). Recently, these isotopic effects have been studied from frequency modulation of the HHG spectrum [131, 132]. However, the full structural and dynamical information is imprinted in both the intensity and phase, so the phase of HHG emission is also important to know. To
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To our best knowledge, only two studies focused on observing the isotopic effect from $H_2$ and $D_2$ by relative phase measurement: from mixed gas in a single gas cell [114] and a spectral phase measurement [115]. The mixed gas technique limited to only a single point in the interferogram and the resolution is not known. It allows observing the magnitude of the phase only [114]. Moreover, the experimental errors of those phase measurements were quite large [114,115], so it is hard to recognize the phase shift precisely. In this thesis, we report the experimental measurement of the relative phase of high harmonics generated from $H_2$ and $D_2$ isotopes by an all optical interferometric technique. Our technique is robust in few ways such as we do not need to calibrate the gas pressure to ensure equal gas densities for both gases in the HHG interaction region. The zeptoseconds resolution of the Gouy phase interferometer allows extracting the relative phase shift very precisely. In addition, the sign of the phase can be is known.

4.4 Derivation of relative phase shift

This section describes the derivation of relative high harmonic phase shift by using the Gouy phase interferometric technique. As we have demonstrated in the previous chapter, when same gas is used in top and bottom jets of the interferometer, the phase difference between the two XUV pulses mainly arises due to the Gouy phase difference between these two jets and the value of phase shift depends on the jets’ separation and harmonic order following the relationship,

\[ \Delta \phi = q \Delta \phi_{Gouy} = q \tan^{-1} \left( \frac{\Delta z}{z_R} \right). \]  

The advanced Gouy phase interferometer is able to measure the intrinsic phase difference between two atoms or molecules. In this situation, the coherent XUV radiations observed on the detector will impose an additional species dependent phase shift along with the Gouy phase shift. Our goal is to extract this inherent species dependent phase from the acquired HHG spectrum/signal. In this section, we describe how to extract this phase shift by the Gouy phase interferometer technique. Here, we will limit our discussion to $H_2$ and $D_2$ isotopes although the basic principle
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The electric field of the HHG signal generated from $H_2$ gas in top jets in figure 4.2 for the $q^{th}$ harmonic order is

$$\vec{E}_{H_2} = E_{H_2} e^{i(q\omega t + q\phi_{Gouy1} + \phi_{H_2})}, \quad (4.2)$$

here, $E_{H_2}$ is maximum field amplitude, $\phi_{Gouy1}$ and $\phi_{H_2}$ are the Gouy phase at the top jet position and intrinsic phase of $H_2$ molecules, respectively. Similarly, the electric field of the HHG signal generated from bottom jet with $D_2$ gas is

$$\vec{E}_{D_2} = E_{D_2} e^{i(q\omega t + q\phi_{Gouy2} + \phi_{D_2})}, \quad (4.3)$$

where $E_{D_2}$ is maximum field amplitude, $\phi_{Gouy2}$ and $\phi_{D_2}$ are the Gouy phase at bottom jet position and intrinsic phase of $D_2$ molecules, respectively. If both jets are ON, two HHG pulses will be generated from top ($H_2$) and bottom ($D_2$) jet with single laser pulse and the field will be the coherent sum of these two electric fields of equation 4.2 and 4.3

$$\vec{E}_{H_2D_2} = \vec{E}_{H_2} + \vec{E}_{D_2}. \quad (4.4)$$

In terms of intensity, the irradiance of the sum of these electric fields is

$$I_{H_2D_2} = I_{H_2} + I_{D_2} + c\epsilon Re \left[\vec{E}_{H_2} . \vec{E}_{D_2}\right] \quad (4.5)$$

$$= I_{H_2} + I_{D_2} + 2\sqrt{I_{H_2} I_{D_2}} \cos (\Delta \phi_{Gouy} + \Delta \phi_{H_2-D_2}),$$

where $\Delta \phi_{Gouy} = \phi_{Gouy1} - \phi_{Gouy2}$ and $\Delta \phi_{H_2-D_2} = \phi_{H_2} - \phi_{D_2}$. Data is then normalized to the in-phase sum of the HHG signals from the $H_2$ jet and $D_2$ jet:

$$N_{H_2D_2} = \frac{I_{H_2} + I_{D_2} + 2\sqrt{I_{H_2} I_{D_2}} \cos (\Delta \phi_{Gouy} + \Delta \phi_{H_2-D_2})}{I_{H_2} + I_{D_2} + 2\sqrt{I_{H_2} I_{D_2}}}. \quad (4.6)$$

Thereafter, if the ordering of gases between top and bottom jets is swapped, i.e. $D_2$ is in the top gas jet and $H_2$ in the bottom gas jet, then the normalized intensity will
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be

\[ N_{D_2H_2} = \frac{I_{H_2} + I_{D_2} + 2\sqrt{I_{H_2}I_{D_2}}\cos(\Delta \phi_{Gouy} + \Delta \phi_{D_2-H_2})}{I_{H_2} + I_{D_2} + 2\sqrt{I_{H_2}I_{D_2}}} \].

(4.7)

The sign of the molecular phases, \( \Delta \phi_{H_2-D_2} \) and \( \Delta \phi_{D_2-H_2} \) will be opposite in this case, i.e. \( \Delta \phi_{H_2-D_2} = -\Delta \phi_{D_2-H_2} \). Finally, by solving equation 4.6 and 4.7, the relative high harmonic phase shift between \( H_2 \) and \( D_2 \) is expressed as

\[ \Delta \phi_{D_2-H_2} = \sin^{-1} \left[ \frac{I_{H_2} + I_{D_2} + 2\sqrt{I_{H_2}I_{D_2}}}{4\sqrt{I_{H_2}I_{D_2}}} \left( \frac{\Delta N_{D_2-H_2}}{\sin(q\Delta \phi_{Gouy})} \right) \right], \]

(4.8)

where \( I_{H_2} \) and \( I_{D_2} \) are HHG yield with \( H_2 \) and \( D_2 \) gas respectively. \( \Delta N_{D_2-H_2} = N_{D_2H_2} - N_{H_2D_2} \) and \( \Delta \phi_{Gouy} \) is Gouy phase difference of the driving laser.

4.5 Experimental setup and measurement protocol

The required instrumentation for this experiment is mainly divided into three parts; (1) The laser system that delivers ultrashort pulses, (2) the Gouy phase interferometer (dual gas jet apparatus) along with the gas handling in the HHG chamber, and (3) the high harmonic detection section. Most of these instrumentations have already been explained in chapter 2, except for the gas handling procedure and fast switching of gases in the jets. In the following section, we will present the details about the gas handling and data acquisition protocol.

4.5.1 Delivering and switching the gases in jets

The dual gas jet apparatus delivers the gases into the HHG chamber. For species dependent intrinsic phase extraction as discussed in section 4.4, swapping the gases between the jets is essential. In addition, switching the gases will also eliminate the intensity dependent phase matching effect (such as dipole phase), effects due to the position difference of the jets within the laser focus. Swapping of the gases between the jets is implemented and controlled by a custom designed LabVIEW code and it makes the data acquisition procedure easier and faster.

Figure 4.3 illustrates the details of the gas handling and delivery into the HHG
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Figure 4.2: Experimental setup for relative phase shift measurement between $H_2$ and $D_2$. The gas jets are placed face to face with each other called top and bottom jet and a separation $\Delta z$ between them along the laser propagation direction. The two HHG pulses generate from $H_2$ and $D_2$ from the two gas jets by single laser beam, propagate, disperse by the flat field grating inside the XUV spectrometer and finally the spectral image is acquired by a CMOS camera. The two XUV pulses exhibit a phase difference with a combination of Gouy phase of the driving laser and the species dependent phase difference between $H_2$ and $D_2$. 

$$E_{H_2} = E_{H_2} e^{i(q\omega t + q\phi_{Gouy} + \phi_{H_2})}$$

$$E_{D_2} = E_{D_2} e^{i(q\omega t + q\phi_{Gouy} + \phi_{D_2})}$$

800nm, 9 fs, 450µJ, 1kHz
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chamber. The $H_2$ and $D_2$ gases are supplied from individual cylinders. The gas flow is controlled through the Swagelok ball valves $V_1$, $V_2$, $V_3$, and $V_4$. Depending on the measurement requirement, either $V_1$ and $V_4$ or $V_2$ and $V_3$ are kept open. The pressure controllers 1 and 2 are the finely controlled needle valves (Model: Edwards LV10K) that precisely control the gas pressure. The pressure in each jet is kept at 100 Torr and measured individually by the two capacitance manometer pressure gauges (model: MKS Baratron 626 and 122A), each of them is connected with the needle valve controllers. The length of the gas lines from the pressure gauge to the jets is kept the same so that each jet experiences similar pressure. Each of the gas jets is connected with two pulsed micro valves with the configuration as shown in figure 4.4. One of them is connected with $H_2$ and another one with $D_2$ gas. The micro valves are energized with a solenoid coil and its working principle has already been discussed in chapter 2. Depending on the measurement requirement one of these valves is open while the other one is kept closed.

4.5.2 Synchronization of experimental apparatus with laser pulse

The micro valves and camera trigger delay are synchronized with the 1 kHz repetition rate of the laser via an FPGA reconfigurable I/O module (model: PCIe-7851). Figure 4.5 illustrates the schematic of synchronization of the experimental devices with the laser pulses. The timing and sequencing of micro valve openings are controlled through a custom written LabVIEW code. The camera link interface (NI 199745A-05 PoCL, MDR to SDR, 5M) establishes fast communication to the frame grabber device for image acquisition from the camera. With all these devices working in combination, a full set of data of 6 spectra [figure 4.7] is saved in a single .dat file that can later be analyzed in MATLAB. The inset of figure 4.5 depicts the timing diagram where $t_v$ and $t_c$ are the trigger delays of micro valve and camera, respectively, with respect to the laser pulses. The HHG yield is optimized by varying the delay between laser pulse and micro valve openings. It is observed that the maximum yield can be obtained at $\sim 700 \mu s$ trigger delay.
Figure 4.3: Schematic of gas handling through micro valves into the gas jets. There are two micro valves attached to each gas jet and one is connected with \( H_2 \) gas and another one with \( D_2 \) gas lines. Depending on the measurement requirement either of the valve corresponding to each jet is opened up and gas enter into the generation chamber through the gas jet. The \( V_1, V_2, V_3 \) and \( V_4 \) are the Swagelok ball valves. The pressure controller 1 and 2 are fine controlled needle valves and capacitance manometer pressure gauges measure gas pressure. The bottom jet is attached with the fixed mount and top jet is free to move in three degrees as the top jet mount is attached with a three axis mechanical translator.
Figure 4.4: Two micro valves with different gases are connected to each gas jet. This configuration facilitates to alter the gases in the jet according to the measurement requirement.

Figure 4.5: Schematic of devices combination and synchronization of all experimental apparatus with laser pulse. Micro valve and camera are triggered with corresponding input laser pulse. Trigger delay is given by the user through LabVIEW code. The MVC 1 software controls the working condition such as open time of the micro valves. Each CMOS output frame is transfer through camera link cable and frame grabber allow high speed digital imaging. (Inset) 40 MHz FPGA clock is employed for the timing of micro valves and CMOS camera triggering. The timing jitter of the 40 MHz FPGA clock is 25 ns at most and does not affect the HHG condition as the FPGA clock is synchronous with 1 kHz repetition rate laser pulse. Figure is adopted from [91].
4.5.3 Measurement protocol and data acquisition

The measurement protocol can be divided into two main steps:

1. Determine the optimum gas jets separations for intrinsic phase shift measurement from gas jet separation vs intensity data.

2. Measure \( \Delta N_{D_2 - H_2} \) of equation 4.8 at the separations optimized from step 1.

Determining the Gouy phase and the optimum jet separation

The first step of measurement is to determine the jet separation where interferometer exhibits the best resolution over the observable spectral range. The best resolution is achieved at a separation where the intensity varies at the largest rate for gas jet separation variation, i.e. \( \frac{dI}{dz} \) is the largest. The data acquisition procedure is identical to the temporal coherence observation as discussed in chapter 3. The HHG yield is measured by varying the gas jets separation. The experimental data on modulation of intensity for 8 harmonic orders as a function of gas jet separation and the fitted curve is shown in figure 4.6. From this figure, we decided to take phase shift measurement at separations 0.63 mm and 1.27 mm. These separations are the 1\(^{st}\) and 2\(^{nd}\) turns, respectively of the mechanical translator that is attached to the top gas jet mount. We chose these separations because the derivative \( \frac{dI}{dz} \propto \frac{dI}{d\phi} \) is reasonably high at these positions. The intensity of a Gaussian beam away from the focus along the laser propagation direction decreases as described by equation 3.4. The Rayleigh length of our laser beam is \( \sim 14 \) mm so at 0.63 mm and 1.27 mm gas jet separations, the intensity difference experienced by the two gas jets is only 0.2% and 0.8%, respectively.

In addition to this, from the fitted curve of figure 4.6, the effective Gouy phase shift (or effective Rayleigh length) for each of the harmonics is measured (see section 4.5.4 for details).

Measuring \( \Delta N_{D_2 - H_2} \)

After optimizing the gas jet separation for the phase shift measurement, we observed \( \Delta N_{D_2 - H_2} \) for these two separations individually. The data were taken for two different gas configurations. Firstly, we use \( H_2 \) in the top jet (before focus) and \( D_2 \) in the
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Figure 4.6: The normalized HHG intensity with $H_2$ gas at varying gas jet separation. Normalized intensity is decreasing as the gas jet separation is increasing from their overlapping position ($\Delta z = 0$). From these data points, we find the position where the intensity variation is the largest for change in jet separation, i.e. $\frac{dI}{dz}$ for all of these harmonic orders. The two dashed lines are the positions where the intrinsic phase shift measurement between $H_2$ and $D_2$ is taken.
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bottom jet (at the focus). The harmonics are generated from both $H_2$ and $D_2$ and the resulting HHG signals are added coherently but with a phase difference due to the Gouy phase of the driving laser and the intrinsic phase difference between $H_2$ and $D_2$ molecules. At the same time HHG intensity with individual gas jet on is also measured in order to normalize the data of equation 4.6. Therefore, three images are captured for each configuration. Data normalization procedure has been explained in chapter 3. Secondly, we swap the gases by opening the alternative micro valve of the corresponding gas jet, i.e. $D_2$ in the top jet and $H_2$ in the bottom jet. Thus, a set of 6 spectra is taken to get $\Delta N_{D_2-H_2}$ of equation 4.8. Figure 4.7 (a) shows these HHG spectra at 0.635 mm gas jet separation and 4.7 (b) shows the images that reveals the difference in harmonic emissions with increasing harmonic order for the above mentioned gas configuration.

4.5.4 Data analysis

The acquired data is processed and analyzed using MATLAB. For each of the spectra shown in figure 4.7, the data points around each harmonic peak are plotted. The peak intensity is determined by fitting these data points by a Gaussian function using a least square fitting tools of MATLAB. The fitting function is

$$f(x) = a \exp \left( \frac{-(x-b)^2}{2c^2} \right)$$ (4.9)

here $a, b$ and $c$ are the fitting parameters. The peak amplitude of the harmonic signal is given by the fitting parameter $a$. From these peaks the normalized intensities as described by equations 4.6 and 4.7 are calculated. The fitting procedure estimates $1\sigma$ (68%) confidence bound to quantify the uncertainties that calculate the standard error. As $N_{H_2D_2}$ is a function of $I_{H_2}, I_{D_2}, I_{H_2D_2}$ and corresponding error is the combined uncertainty of these $\delta N_{H_2D_2}(\delta I_{H_2}, \delta I_{D_2}, \delta I_{H_2D_2})$. Thus, the error bar of $\Delta N_{D_2-H_2}$ is obtained by the propagation of errors and is defined as

$$\delta(\Delta N_{D_2-H_2}) = \sqrt{(\delta N_{H_2D_2}^2 + \delta N_{D_2H_2}^2)}.$$
Figure 4.7: (a) The HHG yields difference between $H_2$ and $D_2$ and combination of them at 0.63 mm jet separation. Each spectrum is an average of 200 images and every spectrum is an integrated HHG signal from 100 laser shots. The ratio of HHG yield increases with harmonic order. The HHG yield measured from individual $H_2$ and $D_2$ gas is also shown here. (b) Raw HHG images corresponding to the top two spectra of (a). Blue represents the weakest signal and red represent the strongest.
Next, the effective $\Delta \phi_{Gouy}$ for each harmonic order is obtained from the normalized intensity vs separation data of figure 4.6. These data are fitted with a decaying cosine function as

$$f(x) = W \exp^{-yx} \cos(Zx) + C$$

where $W$, $Y$, $Z$ and $C$ are the fitting parameters and the $'Zx'$ gives us the $q \Delta \phi_{Gouy}$. Finally, the total error bar of phase shift between $H_2$ and $D_2$ is the propagation error and defined as

$$\delta \phi_{D_2-H_2} = \sqrt{\delta_2^2 + \delta_{\sin(q \Delta \phi_{Gouy})}^2}.$$  

4.6 Experimental results and discussions

4.6.1 With 9 fs driving laser pulses

The high harmonics are generated by a horizontally polarized 1 kHz repetition rate 9 fs duration laser pulses and the estimated peak intensity of the pulse is $\sim 5 \times 10^{14}$ W/cm$^2$. Figure 4.8 shows the relative HHG phase of hydrogen isotopes from H23 to H37. It is observed that the phase shift between $H_2$ and $D_2$ is increasing monotonically as a function of the harmonic order. The measurement is taken at two separations between the gas jets to check for consistency. The results show that the extracted HHG phase shift is similar for both separations. However, at 1.27 mm separation, the phase shift for H35 and H37 is not shown here because at this distance the XUV emission at those frequencies undergo destructive interference (see figure 4.6) and thus $\frac{dI}{dz} \propto 0$. For this reason, extracting the phase shift using the Gouy phase interferometric technique at this points no longer works. In addition, the same measurement have been performed (negative phase shift of the figure 4.8) by exchanging the gases in the micro valves corresponding to each jet - this measurement corresponds to measuring the phase for $H_2$ in respect to $D_2$. This measurement is taken to verify any systematic errors from micro valves and pressure differences that might affect our results. The error bars are the standard error of 200 measurements. The black points are the extracted phase shift when both jets have $H_2$ gas and zero phase differences are expected and observed. The cyan diamond points are the theoretical result obtained by the numerical solution of non-Born-Oppenheimer TDSE equation. The calculation has been performed at different laser intensities and
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it is shown that the calculated phase shift is not very sensitive to the laser intensities. The result shown in the figure 4.8 is an average of 4 different laser intensities, i.e $1 \times 10^{14} \text{ W/cm}^2$, $2 \times 10^{14} \text{ W/cm}^2$, $3.6 \times 10^{14} \text{ W/cm}^2$ and $1 \times 10^{15} \text{ W/cm}^2$.

Figure 4.9 shows the phase shift that is averaged over both separations and reverse gas configuration of figure 4.8. The phase difference is $180 \pm 8 \text{ mrad}$ for $H_2^{3\text{H}}$ and it increases to $228 \pm 44 \text{ mrad}$ for $H_3^{7\text{H}}$. The corresponding time delay between emissions from these two isotopes is given by

$$\Delta t_{D_2-H_2} = \frac{\Delta \phi_{D_2-H_2}}{\omega_q}$$

(4.11)

where, $\omega_q$ is the angular frequency of the $q^{th}$ harmonic order. The relative emission delay from $D_2$ is about 3 attoseconds delayed in respect to $H_2$ and this delay is almost the same (within experimental errors) for all the observable harmonic orders. The right axis (red points) of 4.9 shows the emission delay calculated from the phase shift. The sign of this delay is positive, meaning that the heavy isotope $D_2$ emits later than $H_2$.

**Numerical simulations**

In order to interpret and understand the experimental results a comprehensive theoretical analysis have been preformed. Our theoretical collaborators are Prof. Feng He and Dr. Wanyang Wu from Shanhai Jiao Tong University, China [133]. The simulation is performed by solving the non-Born-Oppenheimer time dependent Schrödinger equation (NBO-TDSE) for all four particles [134]. The laser parameters such as pulse duration and intensity are kept close to the experimental conditions. The simulation is performed considering the dynamics of two electrons coordinates $(x_1, x_2)$ and the two nuclei (internuclear separation, R) but the nuclear motion is restricted to the laser polarization direction. At the same time, the indispensable electron-nuclei coupling is treated fully, rather than within the Born-Oppenheimer approximation. The simulations are in very good agreement with the measurements. While such agreement is encouraging, further analysis is needed to understand the physical origin of the observed emission delays. To that end we compared the dipole density distributions for the two isotopes. The dipole density distributions for the
Chapter 4. Relative phase and attosecond emission delays for HHG from molecular hydrogen isotopes

Figure 4.8: The high harmonic phase shift of $D_2$ relative to $H_2$ with a 9 fs, 800 nm laser pulse from H23 to H37 measured at two different gas jet separations; 0.63 mm (red) and 1.27 mm (blue). The measured phase is increased monotonically with harmonic order. The negative phase corresponding to the $H_2$ phase shift relative to $D_2$. This measurement taken under the same experimental condition except the gases are swapped in jets passing through the alternating micro valves. The zero phases (black points) are observed when $H_2$ gas is in both jets. The error bars are the standard error of 200 measurements. The cyan diamond points are the theoretical result obtained by solving the non-Born-Oppenheimer TDSE.
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Figure 4.9: The left axis shows the relative phase between $H_2$ and $D_2$ (blue points) by averaging the results from both separations and reversing gas configurations of figure 4.8. The right axis is the emission time delays of the corresponding phase difference (red points). The harmonic emission from $D_2$ is $\sim 3$ attoseconds delayed relative to $H_2$ for all these harmonic orders.

$25^{th}$ harmonic order for $H_2$ and $D_2$ are shown in figure 4.10. The dipole density difference at small internuclear separations seems to be responsible for the phase difference. Figure 4.11 (a) and (b) depict the R-dependent dipole density in frequency distribution, $|d(\omega, R)|^2$ where $d(\omega, R)$ is the Fourier transformation of $d(t, R)$. This dipole distribution in R coordinate is calculated by

$$d(t, R) = -\int \int \psi^*(x_1, x_2, R, t) \left| \frac{\partial V}{\partial x_1} \right| \psi(x_1, x_2, R, t) dx_1 dx_2$$  \hspace{1cm} (4.12)$$

where $\psi$ is the wavefunction and $V$ is the potential energy. The short and long trajectories both are included in TDSE simulation. Thus, the phase difference contribution from the short and long trajectories is further analyzed. Figure 4.11(c) presents the time frequency analysis from $D_2$ molecules with single cycle 1000 nm laser pulse. It shows that the phase difference is mainly contributed by the short electron trajectories. It has previously been observed that the intensity of long trajectory is weaker for small molecules such as $H_2$ and $D_2$ due to their faster nuclear dynamics [135]. In general, HHG spectrum originating from the long trajectories...
Chapter 4. Relative phase and attosecond emission delays for HHG from molecular hydrogen isotopes

Figure 4.10: Real and imaginary part of dipole density for $H_2$ and $D_2$ of 25th harmonic order. Here, x axis corresponds to the internuclear separation and y axis corresponds to electronic coordinate [133].

is more diffuse. From the HHG spectrum that we measured (figure 4.7 (b)), it also seems that the on-axis short trajectories give a dominant contribution.

To better understand the origin of the isotopic phase shift, numerical simulation with SFA [136] and SAE [130] approximation were also performed. These analyses helped us to understand the contributions from various factors (electron-electron, electron-nuclei interaction) responsible for the observed phase shift. We know that in SFA, only the ionized electron is taken into account, while its interaction with the ion core is neglected. In reality, the laser field not only acts on the ionized electron but also on all other bound electrons in the molecular ions. In addition, all the electrons in the molecules are correlated and they interact with each other. In other words, the tunnel ionized electron interacts with the remaining electrons of the molecular ion and it will again interact with the bound electron of the ion at the time of recombination.

To confirm the importance of electron-electron interactions during the HHG process, the SAE approximation model was also studied. That model included only one (active) electron while the other electron was approximated by an effective potential. To study the effect of the long range Coulomb potential, our theory collaborators also performed the NBO-TDSE simulation with a short range electron
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Figure 4.11: Dipole in R dependent frequency distribution $|d(\omega, R)|^2$ (a) $H_2$ and (b) $D_2$. It is shown that $D_2$ is emits at smaller internuclear distance, R compared to $H_2$. (c) the time frequency analysis of $D_2$ with a 1000 nm, single cycle laser pulse to see the contribution of short and long trajectories. The short trajectories corresponds to times $< 215$ a.u. and long trajectories to times $> 215$ a.u. [133].

- potential. It was observed that the NBO-TDSE with the screened electron-electron potential gives reduced phase shift and it is close to the phase difference obtained with the SAE model figure 4.12. The screened potential between the electrons of $H_2/D_2$ is defined as

$$V(x_1, x_2)_{\text{screened}} = V(x_1, x_2) \exp\left(-\frac{(x_1-x_2)^2}{m}\right)$$  \hspace{1cm} (4.13)

where m is the potential energy range in atomic unit. From all these numerical analyses SFA, SAE and NBO-TDSE, we can conclude that the Coulomb interaction between electron and ion during the electron acceleration in the continuum as well as the electron-electron interaction play a significant role on the observed phase shift between $H_2$ and $D_2$. The nuclear motion in the $H_2^+$ or $D_2^+$ ground state during tunnelling and recombination process can affect the electron electron correlation. All these results from the numerical simulations are shown in figure 4.12. The SFA simulation reveals that nuclear motion and electron motion have opposite effect on energy dependence of the isotopic phase shift - for nuclear motion the phase difference decreases with harmonic order, while for electron motion it increases. While the overall SFA phase shift is nearly energy independent, in agreement with our experimental observations, its value is much lower than the measured one. Kanai et
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Figure 4.12: HHG phase shift between $H_2$ and $D_2$. (a) Phase shift from the contribution of nuclear movement only (SFA model). (b) Phase shift from the contribution of electron movement only (SFA model). (c) Phase shift from the contribution of nuclear and electron movement both (SFA model). (d) Non-Born-Oppenheimer TDSE at varying electron-electron potential, $V(x_1, x_2)_{\text{screened}} = V(x_1, x_2) \exp\left(-\frac{(x_1-x_2)^2}{m}\right)$, $m$ is the potential energy range and comparison with SAE model [133].

al. relates the phase difference due to the action of ionization potential that depends on the internuclear separation [114]. Hassler et al. compared the experimental results with SFA model and concluded that electron dynamics in the continuum does not effects the phase and the phase only comes from the evolving nuclear wave packet during the recombination step [115]. We conclude from our experimental results and theoretical modelling that SFA fails to capture the isotopic emission delays and correct representation of both electron-nuclear interaction potentials during electron acceleration in the continuum and electron-electron interaction is essential for quantitatively accurate modelling of this effect.

4.6.2 With 50 fs driving laser pulses

The phase difference of HHG emissions between $H_2$ and $D_2$ with a multi-cycle (50 fs) laser pulse has also been measured. The estimated peak intensity of the
Chapter 4. Relative phase and attosecond emission delays for HHG from molecular hydrogen isotopes

Figure 4.13: Optimization of the gas jet separation for the phase shift measurement from 50 fs, 800 nm laser pulses. The two dashed lines are drawn to show the resolution at these separations. Unlike 9 fs pulses, the high phase resolution is impossible to achieve at 1.27 mm separation as the beam parameter has been changed for 50 fs pulses. Thus, we measured the phase shift only for gas jet separation $\Delta z = 0.635$ mm.

Multi-cycle pulse at the focus is $\sim 3 \times 10^{14} \text{ W/cm}^2$. As we have mentioned in chapter 3, the presence of astigmatism at the driving laser focus with 50 fs pulse gives us a different Rayleigh length that changes the fringe periodicity upon gas jet separation. Figure 4.13 shows the temporal coherence from H23 to H35. Due to the shorter Rayleigh length, the Gouy phase difference upon separation varies faster than that we observed with 9 fs pulse. From this figure, we find the optimum separation where $\frac{dI}{dz}$ is highest for all the harmonic orders (dotted line of figure 4.13). In this case, phase difference is measured at 0.635 mm gas jet separation only. The Rayleigh length of our multicycle laser beam is $\sim 8$ mm so at 0.63 mm gas jet separation, the intensity difference experienced by the two gas jets is only 0.6%.

The HHG spectra for $\Delta N_{D_2-H_2}$ measurement are shown in figure 4.14. The
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Phase shifts and the corresponding emission delays between $H_2$ and $D_2$ are shown in figure 4.15. Compared to 9 fs laser pulses, the phase shift with the 50 fs pulses is larger from H23 to H35. The phase difference is $225 \pm 10$ mrad for H23 and increases monotonically to $340 \pm 38$ mrad for H35. The corresponding delay is about 4 attoseconds (within the errorbar) for all of the harmonic orders - that is 1 attosecond more than that of the 9 fs pulses. While that difference is small, it is statistically significant (exceeds the estimated experimental errors).

What can be a reason for the larger phase differences measured with long multicycle laser pulses? First of all, the possibility of target molecule alignment is not negligible within the duration of the 50 fs pulses. Moreover, the population of the nuclear wavepacket on the higher excited $2p\sigma_u$ state starts to become significant after 5 fs and 10 fs for $H_2^+$ and $D_2^+$, respectively (Figure 3 in [137]). In $2p\sigma_u$ state, the internuclear separation increases much more faster than that of $1s\sigma_g$ state. This leads to a higher HHG intensity ratio between $H_2$ and $D_2$ [137,138]. For the same reason, we are expecting that the contribution of higher exited ($2p\sigma_u$) state along with the ground ($1s\sigma_g$) state can results in larger phase difference for the driving laser multi-cycle pulses.

4.7 Summary

This chapter presented measurements and simulations of the relative phase shift (emission delay time) of HHG emissions between hydrogen molecular isotopes, i.e. $H_2$ and $D_2$. The Gouy phase interferometric technique was used for experimental measurements and the numerical solution of NBO-TDSE was used for simulations. The experimental protocol, data acquisition and analysis have been described in detail. We measured the relative HHG phase between $H_2$ and $D_2$. The experiment was performed with 9 fs and 50 fs driving laser pulses. It has been shown that, for both laser pulses, the phase difference increases monotonically as a function of harmonic order but phase shift is higher and increases faster with harmonic order for 50 fs pulse compared to the 9 fs pulse. The population at the higher excited state of $H_2^+/D_2^+$ ions become significant during the 50 fs pulse duration. Thus, the high
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Figure 4.14: The HHG spectrum at different configurations of $H_2$ and $D_2$ gas with 50 fs laser pulses.

Figure 4.15: Relative high harmonic phase shift between $H_2$ and $D_2$ as a function of harmonic order with 50 fs pulse (left axis). The phase shift is increasing monotonically with harmonic order. The corresponding emission delays calculated from the observed phase shift (right axis). The harmonic emission from $D_2$ is $\sim 4$ attoseconds delayed than the $H_2$ molecules.
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harmonic emitted from $H_2^+/D_2^+$ ions populating at the higher excited $2p\sigma_u$ state along with the ground $1s\sigma_g$ state may contribute to the higher phase shifts with 50 fs pulses. The non-Born-Oppenheimer TDSE calculation have been performed to validate the experimental results and the theory successfully reproduced the experimental phase shifts obtained from 9 fs pulses. In addition, comprehensive numerical calculations along with SFA and SAE approximation were carried out by our theory collaborators to uncover the underlying mechanisms responsible for the measured phase difference. It was determined that correct accounting for both electron-nuclear and electron-electron interaction with full long-range Coulomb potentials for both is essential for quantitatively accurate modelling of these isotopic phase shifts. This interferometric technique has opened up a new direction for high-precision measurements of very small HHG phase shift and attosecond emission delays from two high harmonic generating media.
HHG phase shift from methane isotopes

In this chapter, we have extended the isotopic intrinsic HHG phase shift measurement from the simplest $H_2$ to more complex polyatomic molecules methane ($CH_4$) and deuterated methane ($CD_4$). To date most of the experiments on HHG dealt with simple diatomic and triatomic molecules such as $N_2$, $H_2$, $CO_2$ and $N_2O$ [76, 131, 139, 140]. So far, very few works focused on polyatomic molecules either theoretical [141–143] or experimental [66, 75, 144]. In poly-atomic molecules, the interplay of several dynamical effects can be involved during short evolution time in HHG process. The full ab initio theoretical modeling to simulate HHG processes in complex molecular systems like methane is still not available.

A pioneering experiment by Baker et al. provides the first direct experimental evidence of $CH_4^+$ proton motion within the short evolution time during electron travel in the continuum in HHG process by comparing the high harmonic yield from methane isotopes [66]. Later, these experimental results were modelled theoretically in order to analyse the nuclear structural rearrangement [141,145]. Patchkovskii et al. developed an analytical theory to calculate the nuclear autocorrelation function of 15 small molecules and found the largest isotopic effect between $CH_4$ and $CD_4$ [141]. Most recently they have published a more rigorous theoretical analysis of this isotopic effect [143]. There is also an experimental observation of the relative phase shift between successive harmonic orders from methane isotopes from $H13$ to $H23$ by the RABBITT technique [146].

In this chapter, we describe a measurement of the relative phase shift for harmonics $H23$ to $H31$ of methane isotopes by Gouy phase interferometry. To the best of our knowledge this is the first experimental observation of the relative high harmonic phase shift between these hydrocarbon isotopes by an all optical method. The section
Chapter 5. HHG phase shift from methane isotopes

5.1 presents a brief discussion about the structure of methane and its isotopes. In section 5.2, high harmonic generation from \( CH_4 \) and the temporal coherence of the HHG spectra measured by the Gouy phase interferometer has been presented. The next section describes the experimental results of relative phase measurement and interprets the results along with the theoretical support. The chapter’s conclusions are given in section 5.4.

5.1 Structure of methane and deuterated methane

Methane is a primary component of natural gas and substantial contributor to the greenhouse effect on earth. It is the most abundant molecule after nitrogen in Titan [147] and also an important molecule of most neutral and ionic species in Titan atmosphere. \( CH_4 \) is the simplest polyatomic hydrocarbon molecule with tetrahedral geometrical structure as shown in figure 5.1. The central carbon atom has 4 valence electrons and thus 4 hydrogen atoms make the covalent bonds to complete its octet. For \( CD_4 \), these four hydrogen atoms are replaced by deuterium atoms. In fact, methane has total 15-6=9 fundamental modes of vibration. The bond angle between hydrogen atoms is 109.5° and it gives the molecule the tetrahedral geometry. It is well known that methane changes from tetrahedral \( T_d \rightarrow C_{2v} \) symmetry [66,148] by structural deformation in the \( CH_4^+ \) cation by Jahn-Teller symmetry breaking [148] as shown in figure 5.2. Table 5.1 presents the comparative structural properties of \( CH_4 \) and \( CD_4 \).

Although earlier studies showed that HHG spectra are attributed solely to the highest occupied molecular orbital (HOMO) of molecules [70], later studies demonstrated that multiple molecular orbitals can contribute to the HHG emission [127,139,149]. The electronic configuration of tetrahedral methane has three degenerate HOMOs (HOMO-1, HOMO-2 and HOMO-3) and their energies are close to each other. For example, the ionization potential difference between HOMO-1 (12.615 eV) and HOMO-2 (12.95 eV) is very small, so the ionization from HOMO-1 is not negligible [146]. Moreover, from a Franck-Condon (FC) factor analysis, it is found that when \( CH_4 \) (or \( CD_4 \)) is ionized, two vibrational transition modes (E and \( A_1 \)) can be
Table 5.1: Comparative structural information of $CH_4$ and $CD_4$ [150,151].

<table>
<thead>
<tr>
<th>Material</th>
<th>$CH_4$</th>
<th>$CD_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular structure</td>
<td>tetrahedral</td>
<td>tetrahedral</td>
</tr>
<tr>
<td>Ionization potential (eV)</td>
<td>12.615</td>
<td>12.670</td>
</tr>
<tr>
<td>Molecular weight (g/mol$^{-1}$)</td>
<td>16.04</td>
<td>20.07</td>
</tr>
</tbody>
</table>

Figure 5.1: The tetrahedral structure of methane and deuterated methane. In $CH_4$, carbon atom make sigma bond with 4 hydrogen atoms to fill the octet and in $CD_4$ these 4 hydrogen atoms are substitute by deuterium atoms [152].

excited [145] as shown in figure 5.3. The E symmetry modes bring the molecules towards a symmetry plane and $A_1$ symmetry mode elongates the C-H (C-D) bond lengths. The contribution from both of these modes drives the $CH_4^+$ (or $CD_4^+$) ions to $C_{2v}$ symmetry.

5.2 HHG from Methane

A fundamental challenge in generating high harmonics from hydrocarbon $CH_4$ molecules is its comparatively low ionization potential that limits the cut-off energy and spectral range of high harmonic emission. That is why HHG experiments from hydrocarbon targets are generally conducted with mid-infrared laser pulses [153,154]. The low ionization potential also limits the laser intensity as saturation of ionization is reached easily. The ionization potential, $I_p$ of methane is 12.615 eV that is lower than that of Ar ($I_p$=15.8 eV) or $H_2$ ($I_p$=15.43 eV). We observed the high harmonic
Figure 5.2: The molecular structure of $CH_4$ to $CH_4^+$. It is predicted that after ionization the $T_d$ structure of $CH_4$ will evolve into $C_{2v}$ geometry in $CH_4^+$ cation. Figure is adopted from [66].

Figure 5.3: (a) The three degenerate HOMOs of $CH_4$ molecular orbitals. These orbitals are appeared as symmetrical tetrahedral configuration. (b) The characteristic vibration of $CH_4$. The Franck-Condon factor analysis gives two dominating vibrational modes that drive the methane $T_d$ symmetry structure to $C_{2v}$ symmetry. The E mode brings the molecule towards a plane and the $A_1$ mode stretches the C-H bond lengths. Figure is adopted from [145].
Chapter 5. HHG phase shift from methane isotopes

Figure 5.4: Comparison of HHG spectrum from Ar and $CH_4$. The lower $I_p$ of methane limits the HHG cut-off energy so only 6 harmonic orders can be observed while 9 harmonic orders can be seen from atomic Ar gas with the same experimental conditions.

spectrum from the Ar and $CH_4$ with the same experimental conditions. Figure 5.4 represents the comparison of the HHG spectra from Ar and $CH_4$ with the same experimental parameters measured on the same day. The lower $I_p$ of methane limits the harmonic cut-off energy and we can hardly observe 6 harmonic orders from H23 to H33 while in case of Ar 9 harmonic orders can be observed.

5.2.1 Temporal coherence of consecutive harmonics

The temporal coherence of consecutive harmonic orders from $CH_4$ target molecule using the Gouy phase interferometer is observed and shown in figure 5.5. The fringe visibility upon gas jet separation is very similar to that observed from $H_2$ with the multi-cycle laser pulses. The harmonic yield is changing from constructive (at overlapping gas jet position) to destructive and returns back to constructive interference again at larger gas jet separation. It is also clear that the periodicity of fringes decreases with increasing harmonic order as the XUV phase shift depends on the Gouy phase shift of the driving laser pulse following the relationship $\Delta \phi =$
Figure 5.5: The observation of temporal coherence of 6 consecutive harmonic orders generated from $CH_4$ with 50 fs pulses. The HHG yield is plotted as a function of gas jet separation when both jet is ON. The fringes periodicity depends on the harmonic order. The H23 undergoes for 1st revival constructive interference peaks at 4 mm while H33 does it at 2.5 mm.

$q\Delta \phi_{Gouy}$, where $q$ is the harmonic order. From this measurement, we optimized the gas jet separation, where the best resolution of the interferometer can be obtained over the observable harmonic spectrum with same manner we did in the previous chapter. After optimization, we decided to take the measurement of intrinsic phase shift at 0.63 mm separation between the gas jets.

5.3 High harmonic phase shift between $CH_4$ and $CD_4$

The experimental setup, data acquisition and processing are very similar to the $H_2/D_2$ phase shift measurement explained in chapter 4. The only difference is the $H_2$ and $D_2$ gas cylinders are replaced by the $CH_4$ and $CD_4$ cylinders. The pressure of each gas is kept at 100 Torr. The experiment is performed with multi-cycle (50 fs)
driving laser pulse and the estimated peak intensity at the focus is $\sim 3 \times 10^{14} \text{W/cm}^2$.

Figure 5.6 shows the HHG spectra taken for the phase shift measurement. A set of 6 HHG spectra are acquired for each measurement and each spectrum is an average of 200 measurements. The red and green spectra are corresponding to the HHG signals acquired from individual $CH_4$ and $CD_4$ gas, respectively. The blue lines are the HHG yields with both gas jets ON. This is the coherent sum of intensities with a phase difference due to the Gouy phase as well as molecular phase between these isotopes. The blue solid line corresponds to the top jet having $CD_4$ and bottom jet having $CH_4$ gas, and the blue dash line is vice versa. It is clear that the ratio of HHG yield between these two spectra as a function of harmonic order increases much faster if we compare the data with those of the $H_2$ isotopes in chapter 4. By normalization of the data set with the HHG signal from individual gases (equation 4.6 and 4.7) and subtraction from one to another, $\Delta N_{CD_4-CH_4}$ is obtained. From this data set, the relative phase shift between $CH_4$ and $CD_4$ is extracted by using the equation

$$\Delta \phi_{CD_4-CH_4} = \sin^{-1}\left[\frac{I_{CH_4} + I_{CD_4} + 2\sqrt{I_{CH_4}I_{CD_4}}}{4\sqrt{I_{CH_4}I_{CD_4}}} \left(\frac{\Delta N_{CD_4-CH_4}}{\sin(q\Delta \phi_{Gouy})}\right)\right], \quad (5.1)$$

Here, $I_{CH_4}$, $I_{CD_4}$ are the high harmonic yield from methane and deuterated methane respectively. The normalized intensity difference, $\Delta N_{CD_4-CH_4} = N_{CD_4CH_4} - N_{CH_4CD_4}$, where, $N_{CD_4CH_4}$ are the normalized intensity with $I_{CD_4}$ in top jet and $I_{CH_4}$ in bottom jets and $N_{CH_4CD_4}$ is for vice versa. The $q\Delta \phi_{Gouy}$ term is obtained from the fitting curve of the temporal coherence vs gas jets separation figure (section 4.5.4 for detail).

5.3.1 Results and discussions

Figure 5.7 represents the high harmonic phase difference of deuterated methane relative to methane from H23 to H31. It is clear that the phase difference (blue points) increases rapidly as a function of the harmonic order. For H23, the phase shift is $95 \pm 6$ mrad and it increases sharply to $460 \pm 83$ mrad for H31. In comparison with the phase shift observed from hydrogen isotopes, the phase difference between methane isotopes increases at much faster rate with harmonic order (or photon
Figure 5.6: The HHG spectra from $CH_4$ and $CD_4$ with individual and both gas jets ON.

energy). The corresponding emission time delay from the observed phase shift is increased from 1.8 attoseconds for H23 to 6.3 attoseconds for H31.

The molecular weight of $CD_4$ is larger than that of $CH_4$ and thus its nuclear motion is expected to be slower. However, unlike hydrogen, its nuclear motion is not as simple as one dimensional vibration. Rather multiple effects from different electronic degenerate states and nuclear vibration can contribute (discussed in section 5.1) to our experimental observations.

Theoretical analysis

The experimental result has further been validated with theoretical analysis. The cyan square points of figure 5.1 shows the theoretical results of phase difference between the isotopes. These calculations were performed by Dr. Serguei Patchkovskii from Max-Born institute, Berlin, Germany [155]. The simulation model is based on a specialized strong field approximation method where all electrons and nuclei of methane molecule is considered and their interaction are treated quantum mechanically. It is called multiconfigurational strong field approximation with Gaussian nuclear
wavepackets (MC-SFA-GWP) \[143\]. In this simulation no simplification of the dipole matrix element (equation (29) of \[143\]) is considered. It includes nuclear movement and its correlation with all other electrons, the interaction of electrons with laser field at the moment of ionization and in the continuum. However, only short trajectories are taken into account. The calculation is performed with subcycle laser pulse so continuous HHG spectra is observed. The theoretical result agrees well with the experimental phase shift at $2 \times 10^{14} \text{W/cm}^2$ laser intensity. This intensity is close to our experimental estimated intensity. It is anticipated that, this phase difference is due to the difference in field free nuclear dynamics (with the field playing little role beyond clocking the process) of these isotopes.

This measurement supports the evidence that was presented by Baker et al. \[66\] that structural deformation of $\text{CH}_4^+$ ion from $T_d \rightarrow C_{2v}$ geometry is occurring on a sub-cycle timescale of the laser field during the ionization and recombination event of HHG. The tunnel ionized electron spends a specific time in the continuum before it recollides with the parent ion. In the PACER technique, where the ionization step of HHG is considered as pump and recombination step as probe, with only short trajectories considered, the delay between the ionization and recombination increases with the harmonic order \[66\]. For this reason, it can be said that the electron return time with the parent ion is longer for H31 than H23. Thus, structural rearrangement of $\text{CH}_4^+/\text{CD}_4^+$ ion takes place for longer time for H31 than H23. Due to the mass difference between the $\text{CH}_4$ and $\text{CD}_4$, the difference in nuclear rearrangement of these isotopes also increases over the time. That is why the phase difference is increasing with harmonic order.

\subsection*{5.4 Summary}

The experimental observation of HHG phase shift between the methane isotopes is presented in this chapter. The temporal coherence with $\text{CH}_4$ target molecule by Gouy phase interferometer has been tested first. The coherence properties show the similar behaviour that we have observed for $\text{Ar}$ and $\text{H}_2$. The phase shift between the isotopes increases rapidly with harmonic order and the value is $95 \pm 6 \text{ mrad}$ for H23.
Figure 5.7: The left axis shows the phase shift of deuterated methane \((CD_4)\) relative to methane \((CH_4)\) from H23 to H31 measured at 0.63 mm separation between the gas jets (blue points). The cyan squares are the phase shift obtained from the theoretical analysis. The right axis shows the corresponding emission time delay from the observed phase difference (red points).
and increased to $460 \pm 83$ mrad for H31. The experimental result is validated with the theoretical collaboration. The numerical simulation with multiconfigurational strong field approximation with Gaussian nuclear wavepackets (MC-SFA-GWP) is performed and it agrees well with the experimental results. Theoretical analysis predict that the phase difference is due to field free nuclear dynamics of the isotopes. Our results support the assumption that the structural deformation in $CH_4^+$ or $CD_4^+$ ion occurs within the very fast time between the ionization and recombination event in the HHG process. However, due to the lower $I_p$ of methane we can only observe the HHG signal up to H31 order. In the future, extending the experiment to higher laser intensity or mid-infrared driving laser pulses will allow to measure the high harmonic phase in a broader spectral range.
This chapter summarizes the main findings of the thesis and provides a brief discussion on possible future directions.

6.1 Review of research

In this thesis, a highly non-linear phenomenon called the high harmonic generation that occurs with the interaction of intense laser pulse with matter has been investigated. The ultrashort 9 fs duration, 1 kHz repetition rate pulsed laser centered at 800 nm wavelength with peak intensity of $\sim 5 \times 10^{14}$ W/cm$^2$ are obtained by exploiting a number of phenomena such as Kerr-lens mode locking and chirped pulse amplification, self-phase modulation in a hollow-core fiber and subsequent pulse compression by dielectric chirp compensation mirrors. The beam is characterized by measuring the pulse energy, pulse duration, spectral bandwidth, and its confocal parameters such as spot size and Rayleigh range. By focusing this ultrashort laser beam into a vacuum chamber and letting it interact with atomic or molecular gases results in the generation of high harmonic XUV pulses. The generated high harmonic signal is observed and characterised by the detection apparatus consisting of a flat-field XUV spectrometer followed by an MCP image intensifier and CMOS camera detector.

The thesis original content can be divided into three main parts. Firstly, the design and implementation of the advanced Gouy phase interferometer are presented in chapter 3. The interferometer has been improved in several ways compared to its prototype in order to increase its robustness and make it suitable for future application such as extracting the relative high harmonic phase shift between two different gas species. These improvements include redesigning the dual gas jets apparatus in such a way that two different gas species can be alternated between the
two jets by operating two pulsed micro-valves corresponding to each gas jet. The pulsed micro-valves reduce the background pressure in the HHG generation and detection chamber. Moreover, the fast detection apparatus makes the data acquisition process easier and faster. The temporal coherence of HHG in this advanced Gouy phase interferometer is observed by varying the gas jets separation with both 9 fs and 50 fs driving laser pulses. This coherence has been investigated with HHG generated from atomic and molecular target gas media. In addition to this, the ability of controlling the spectral shape of HHG emissions to select a range of harmonics by utilizing this interferometric technique is presented.

The next two chapters describe the relative phase shift measurement of HHG from two molecular isotopes using this interferometric technique. The first experiment targets the simplest molecular isotopes $H_2$ and $D_2$. The details of the phase extraction procedure, data acquisition and analysis are explained in that part. The results show that relative HHG phase shift increases monotonically with the harmonic order (HHG photon energy). It has been observed that the phase shift is $180 \pm 8$ mrad ($225 \pm 10$ mrad) for H23 and increases to $230 \pm 26$ mrad ($340 \pm 38$ mrad) for H35 by 9 fs (50 fs) laser pulses. This phase difference corresponds to a harmonic emission delay of approximately 3 (4) attoseconds between $H_2$ and $D_2$ with 9 fs (50 fs) driving laser pulses. The ab-initio NBO-TDSE simulation validates the experimental results observed with 9 fs laser pulse. The numerical simulation with strong field approximation, single active electron approximation and NBO-TDSE with short range electron-electron potential were also compared with our measured phase differences. The comparison with all these theoretical analyses indicates that the Coulomb interaction between ionized electron and parent ion during the electron acceleration in the continuum as well as the correlation between two electrons of the hydrogen molecule play a vital role to the experimentally observed phase shift.

The final experiment of this thesis is the investigation of HHG phase shift measurement between more complex methane molecular isotopes $CH_4$ and $CD_4$. The result shows that the phase shift between $CH_4$ and $CD_4$ increases rapidly with the harmonic order. The phase shift is $95 \pm 6$ mrad for H23 and increases to $460 \pm 83$
mrad for H31. The nuclear motions of the tetrahedral methane molecule are far more complex compared to the linear hydrogen molecule. It is believed that after ionization, the two dominating vibrational modes (E and $A_1$ symmetry mode) drive the $CH_4^+$ ions to deform from $T_d$ symmetry structure to $C_{2v}$ symmetry. Due to the mass difference between these isotopes their vibrational times are expected to be different. From the PACER technique we know that, if only the short trajectories are considered, the higher the harmonic order the longer time the ionized electron will take to return back to its parent ion. That means that $CH_4^+$ ions will be more deformed for longer time interval for higher harmonic order compared the lower order. As a result, the phase difference between the isotopes is increased with harmonic order.

### 6.2 Future directions

The observation of high harmonic phase shift between the two molecular isotopes has opened up a new avenue in the field of high harmonic spectroscopy. This new approach will help to understand the real time dynamics and structural information of electron and nucleus in atoms and molecules including experimental access to electron-electron correlations. This research can be extended in several ways in the future.

The present experiment is conducted with randomly aligned molecules. In the future, performing the experiment with aligned target molecules can give more detailed information. The molecular spectroscopy by the high harmonic generation is limited to the optical period of driving laser pulse. If we used a longer wavelength (longer optical cycle), midinfrared laser field, electrons will have a longer travel time in the continuum and thus it will trace the nuclear dynamics at a later time. In addition, performing the experiment with atomic isotopes and stereo-isomers can be interesting. The information about the hyperfine structure of atoms can be investigated from the phase shift measurement of atomic isotopes. High harmonic spectra of stereoiosmers are shown to be different [156] so observing the harmonic phase can be helpful to understand these molecular structure and dynamics.
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Bibliography


Appendix A

List of publications and personal contributions

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

   - I assisted preparing and setting up the experiment. I collected, processed and analyzed the experimental data. I prepared the manuscript. This manuscript is from part of chapter 2 and chapter 3 in this thesis.

   - Lead experimentalist. I prepared the experiment, collected data, analyzed data. I am preparing the manuscript. This publication will be from chapter 4 of the thesis.

   - Lead experimentalist. I prepared the experiment, collected data, processed and analyzed the data. I am preparing the manuscript. This publication will be from chapter 5 of the thesis.
Appendix B

Published articles
Advanced Gouy phase high harmonics interferometer

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View the article online for updates and enhancements.
Advanced Gouy phase high harmonics interferometer


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Abstract

We describe an extreme ultraviolet (XUV) interferometric technique that can resolve ∼100 zeptoseconds (10−21 s) delay between high harmonic emissions from two successive sources separated spatially along the laser propagation in a single Gaussian beam focus. Several improvements on our earlier work have been implemented in the advanced interferometer. In this paper, we report on the design, characterization and optimization of the advanced Gouy phase interferometer. Temporal coherence for both atomic argon and molecular hydrogen gases has been observed for several harmonic orders. It has been shown that phase shift of XUV pulses mainly originates from the emission time delay due to the Gouy phase in the laser focus and the observed interference is independent of the generating medium. This interferometer can be a useful tool for measuring the relative phase shift between any two gas species and for studying ultrafast dynamics of their electronic and nuclear motion.

Keywords: high harmonic generation, Gouy phase interferometer, phase shift, temporal resolution

1. Introduction

Extreme ultraviolet (XUV)—soft x-ray light sources based on high harmonic generation (HHG) [1–3] are table-top in size, can have sub-femtosecond pulse duration and could be used for coherent imaging with sub-angstrom spatial resolution. The underlying physics of HHG is well described by the three-step semi-classical model [4]. In the first step, a laser electric field suppresses the potential barrier of an atom or a molecule and a bound electron undergoes tunnel ionization. The ionized electron is then accelerated in the continuum by the driving laser electric field, gaining kinetic energy. Finally, when the electric field reverses its direction, the electron recombines with the excited state parent ion and subsequently emits a coherent XUV photon.

This recollision process occurs every half cycle of the driving laser field resulting in a harmonic spectrum with a number of peaks at odd multiples of the driving laser frequency. In time domain HHG emission corresponds to attosecond pulse trains or, when driven by properly tailored few-cycle pulses, to isolated attosecond pulses [5, 6]. The amplitude, phase and directionality impressed on HHG by the laser field provide a snapshot of the structure and dynamics of the generation medium.

Although intensity of the HHG pulses can readily be measured, a measurement of the phase of the harmonics is still a challenging task because of their very short wavelength. This phase carries important information about the recombining electron and nuclear wavefunction. Interferometry is a common technique to extract the phase of light. The most commonly used interferometers, Michelson or Mach–Zehnder, generate a pair of temporally delayed XUV pulses by splitting the input pulse into two and propagate them along different paths, where the phase difference is introduced before recombining. The stability of the two optical paths due to the air turbulence and mechanical vibrations is a major technical issue limiting the precision and resolution of such measurements. The best temporal resolution achieved by such
measurements to date is 280 zs [7] but this technique is not well suited for XUV light generated with HHG. Another technique that has been used to extract the relative HHG yields for pure and mixed gases in a single gas jet [8–12]. However, this approach requires a very careful calibration of partial gas pressures to ensure same number density for each source. Full temporal characterization of high harmonics XUV pulses was demonstrated from spectral phase interferometry [13]. Recently, harmonic phase was measured from two HHG emissions generated by a single laser beam and by introducing a π phase difference between two parts of this HHG generating beam [14]. However, these methods are not well suited for observing very small phase shifts between two XUV sources using different target gases.

The Gouy phase interferometer generates XUV light from two independent, spatially (along the laser propagation direction) separated gas jets situated within a single Gaussian beam focus [15]. The HHG emissions generated from the two jets have a phase difference which arises due to the Gouy phase variation across the focus. Thus, at a particular gas jets separation certain XUV harmonics could interfere constructively while others may undergo a destructive interference. Moreover, as we have previously demonstrated, this Gouy phase interferometer is capable of measuring few milli-radian phase difference of HHG pulses corresponding to time delays on the order of 100 zs. In this paper, we present a new design for an advanced Gouy phase interferometer that improves the sensitivity over our previous design by a factor of 15. In addition, using pulsed micro valves synchronized with 1 kHz repetition rate laser pulse allows us to reduce background pressure in the HHG generation and detection chamber by a factor of 6 without reducing gas density in the interaction region.

2. Principle of the interferometer

The working principle of the Gouy phase interferometer is illustrated in figure 1. Two spatially separated gas jets are placed along the propagation axis of single Gaussian laser beam focus and an HHG emission is produced in each jet. The emission of an HHG photon depends on the trajectory of the tunnel-ionized electron and the Gouy phase introduces a delay in HHG emission time, $\Delta t$, that results in a phase shift, $\Delta \phi$ between the two XUV pulses. This phase offset results in a constructive and destructive interference between these XUV pulses.

Figure 1. Schematic illustration of the principle of operation of the Gouy phase interferometer. (a) A Gaussian IR laser beam is focused and two jets are placed near the focus. HHG radiation is generated in each of the gas jets and the phase of the HHG pulses depend on the position of the associated generating gas jet. (b) Gouy phase at different locations within the laser focus along laser propagation direction for Rayleigh length, $z_R = 14$ mm. Due to the Gouy phase, there is a phase difference between carrier wave and envelope of driving laser field that turns into $\pi/2$ phase shift over a Rayleigh length ($\approx z_R$). (c) Gouy phase imparts a delay in emission time $\Delta t$ that results in a phase shift, $\Delta \phi$ between the two XUV pulses.
\(\pi/2\) phase shift with respect to a plane wave over a Rayleigh length \(z_R\) as shown in figure 1(b). This geometrical phase shift is referred to as Gouy phase [16] and is experimentally verified for HHG in few-cycle pulses [17]. The Gouy phase is defined as

\[
\phi_{\text{Gouy}}(z) = -\tan^{-1}\left(\frac{z}{z_R}\right).
\]

where \(z\) is the distance from the laser focus along the direction of propagation and \(z_R\) is the Rayleigh length defined as \(z_R = \frac{\lambda^2}{\pi}\) and \(w_0\) is the \(1/e^2\) beam radius at the focus.

The emission phase for a particular harmonic, \(q\), can be expressed by the Lewenstein model [18, 19]

\[
\phi = q\omega t_r - \frac{1}{\hbar}S(p_i, t_r, t_f),
\]

where \(\omega\) is the angular frequency of the driving laser and \(t_r\) is the time taken for the electron to recombine with the parent ion or the recombination time. In the second term, \(S\) is the semi-classical action on the ionized electron, which depends on the canonical momentum \(p_i\), electron ionization time \(t_i\) and recombination time \(t_r\). This semi-classical action term is proportional to the product of the laser intensity and the electron travel time and the third term is the difference in the semi-classical action term.

The electron recombination time \(t_r\) depends on the position of the gas jet in the laser focus and is related to the Gouy phase as

\[
t_r(z) = t_r(z = 0) + \frac{\phi_{\text{Gouy}}(z)}{\omega},
\]

where \(t_r(z = 0)\) is the return time for an electron exactly at the centre of laser focus where there is no influence of the Gouy phase. Thus the total phase difference of the \(q\)th harmonic from two gas jets located at \(z_1\) and \(z_2\) positions in figure 1 is

\[
\Delta\phi = q(\phi_{\text{Gouy}}(z_1) - \phi_{\text{Gouy}}(z_2)) + q\omega(t_i(z_1) - t_i(z_2))
- \frac{1}{\hbar}(S_1 - S_2).
\]

The first term in this expression is the difference in the Gouy phases only, the second term is the difference in the electron travel time and the third term is the difference in the semi-classical action between the two HHG generation sources. The intensity of a Gaussian beam decreases as \(I(z) = \frac{I_0}{1 + (z/l)^2}\), thus near the laser focus intensity will not change significantly and second and third term of this expression will be nearly zero. Equation (4) can be approximated by the first-order Taylor series expansion to find an approximate expression for the phase difference as

\[
\Delta\phi \approx q \frac{d\phi_{\text{Gouy}}}{dz}\Delta z - \frac{d\phi_{\text{Gouy}}}{dz}\Delta z.
\]

For simplicity, electron travel time and semi-classical action terms are combined into \(\phi_{\text{Gouy}}\). This expression implies that a small shift of Gouy phase results in a change in the phase between the two emissions corresponding to the harmonic order \(q\) that is \(q\) times larger. In measurements reported below we keep this phase shift to the range from zero to slightly over \(\pi\) (corresponding to one period of XUV oscillations) in order to avoid significant intensity variations. That allowed us to trace the interference through the first minimum (destructive interference) to the first-order maximum (constructive interference).

3. Experimental details

The laser system is a commercial Quantronix Ti:Sapphire oscillator (Ti-Light) and chirped pulse amplifier (Odin-II) providing a 3 mJ, 1 kHz repetition rate 30 fs pulses centred at 800 nm. A neon filled hollow core fibre spectrally broadens the pulse by self-phase modulation technique that introduces a positive chirp in the pulse while keeping the pulse duration same. Then, a pair of chirped dielectric multilayer mirrors compensates the chirp by introducing negative group delay dispersion and wedges finely tune the chirp and give us 9 fs pulse of energy \(\sim 500\) \(\mu\)J. Finally, the beam is focused into the HHG generation chamber, where the Gouy phase interferometer is installed, by a 750 mm focal length spherical mirror. The focal position can be finely adjusted by a translation stage. As the Gouy phase is a complete geometrical phase mismatch effect, the correct choice and day-to-day measurement of Rayleigh range and confocal parameters are vital for this experiment. The average Rayleigh length is \(14 \pm 1.4\) mm and maximum laser intensity at the focal point is estimated to be approximately \(5.0 \times 10^{14}\) W cm\(^{-2}\).

3.1. Interferometer design

We have redesigned the HHG interferometer presented in [15] to improve the reliability and the phase resolution of the instrument. A particular issue with our prototype interferometer was the requirement to open and close the gas jets manually with leak valves and to wait for a significant amount of time for the stabilization of the pressure. In the new interferometer, we implemented micro valves that actuate electromagnetically and can switch faster than in a millisecond. The use of the pulsed micro valves enabled measurements to be carried out 15 times faster than the prototype version. It is important to keep background pressure in the detection chamber under 10 \(\text{Torr in order to avoid damaging the microchannel plate (MCP) image intensifier. The use of valves reduces background pressure in the generation chamber by a factor of 6 while keeping the gas number density high in the interaction region. Moreover, the old interferometer had a slow phosphor and CCD camera that had 100–200 ms readout time. The new apparatus uses a very fast P-47 phosphor screen that has 400 ns decay time and a CMOS camera with no dead time for readout making data acquisition faster. Through all these improvements the generation, detection and acquisition of HHG spectrum takes less than 1 ms, so a pulse-by-pulse measurement is now possible with this new instrument. While the single-shot capability was not utilized in measurements reported here, it will be essential
for carrier-envelope-phase dependent measurements with phase-tagging we are planning to perform in the future.

### 3.2. Interferometer assembly

The schematic of the Gouy phase interferometer is shown in figure 2. The apparatus consists of two jets, the bottom jet pointing up and fixed in position while the top gas jet points down and it is movable along the XYZ axes by a triple-axis mechanical translator (MDC PSM-1502). The laser beam entering the chamber is aligned to the fixed jet first and then the top jet is translated to align with the laser beam and the fixed jet. Two micro valves are connected to each jet to facilitate the switching of gases according to the measurement protocol. A field programmable gate array (FPGA) enables fast switching of the gas in the jets using the micro valves. The pressure in both gas lines is kept at 100 Torr measured by capacitance manometer pressure gauges. Individual gas lines are plumbed via teflon tubing to each gas valve from their respective cylinders. Swagelok plug valves regulate the required gas species in the jet. Figure 3 depicts the images of individual components of the dual gas jet apparatus. Each gas jet is formed by a stainless steel syringe (Terumo needle: 0.5 mm × 19 mm) attached to the jet holder. The needle’s sharp and unwanted plastic edges are removed by scanning it through the laser output beam focus.

The inner diameter of the needle is ∼200 μm and the laser focus is positioned within 100 μm of the needle’s tip. Thus, the interaction length of gas and the laser is estimated to be ∼300 μm and the average Rayleigh length for the experiment is approximately 14 mm. Such a short interaction length has been chosen in order to minimize the complexity of other phase matching effects and re-absorption of harmonic emission by the generating medium [20].

The timing and sequencing of opening and closing of the micro valves is synchronized with 1 kHz repetition rate laser pulse via FPGA reconfigurable I/O module (PCIe-7851) and controlled through a custom written LabVIEW code as shown in figure 4(a). The modular controller (Gyger MVC1) handles working condition of micro valves such as current, duty cycle via java based MVC-software. The camera link interface (NI 199745A-05 PoCL, MDR to SDR, 5M) establishes fast communication to frame grabber device for image acquisition from camera. Figure 4(b) depicts the timing diagram where $t_v$ and $t_c$ are the trigger delays of micro valve and camera respectively with respect to 1 kHz repetition rate laser pulse. We also monitored HHG yield at three different valve opening durations by varying the delay between laser pulse and valve openings in order to get maximum HHG yield as shown in figure 4(c). Based on this data we kept the delay at ∼750 μs for the rest of the experiment.

![Figure 2. Schematic of Gouy phase interferometer. Top and bottom mounts hold the gas jets. The bottom mount is fixed in position and top mount is movable along three axes by the mechanical translators. Each mount can hold two micro valves, both connected to single gas jet. Gases enter into the HHG generation chamber through the jets. Valves are connected with teflon tube through which gases are supplied from the cylinder. The gas pressure in each line is monitored individually by two capacitance manometer pressure gauges those are placed outside the HHG chamber. In order to ensure same pressure in both gas jets, the distance and configuration of gas line from the pressure gauge to the gas jet are kept the same.](image-url)
After HHG generation, both the fundamental IR and XUV light are co-propagating. However, to analyze the XUV radiation a spectrometer is used. This requires the fundamental IR light to be removed. The IR beam is blocked by a 200 nm thick Al filter (Lebow: 0.1Al-0.1Al-O-L1.0) that transmits only 20–72 eV radiation. The filtered XUV photons are then spectrally dispersed by a flat field XUV spectrometer (Hettrick Scientific EUV-K) which is identical to our previous spectrometer [15].

The HHG spectrum image intensifier section consists of a double stage MCP coupled with very fast P-47 phosphor (BOS-75-OPT01/DET/P-47). The MCP has electron gain of $10^7$ and imaging area of 75 mm diameter which can capture the whole HHG spectrum. We use macro lens (Zoom 7000 Navitar) to image the spectrum with zero distortion on a CMOS camera (Basler acA2000-340km). The CMOS camera is used instead of CCD as it facilitated a faster read-out time which is important for single laser shot measurements. The layout of full experimental setup is shown in figure 5.

### 4. Results and discussions

We have replicated the results reported in [15] in order to determine the effectiveness of our modifications and upgrade of the new Gouy-phase interferometer. First, the temporal resolution of the interferometer has been estimated through a measurement of the Allan deviation [21]. It characterizes the uncertainty of a measured quantity as a function of the experimental measurement time. By monitoring this dependence the optimum measurement time can be chosen. The overlapping Allan deviation method is used for the Allan deviation estimated in figure 6(b) and is defined as

$$
\sigma_{\text{Allan}}(\tau) = \left( \frac{1}{2(N - 2m)} \sum_{i=1}^{N-2m} (y_i - \bar{y})^2 \right)^{1/2},
$$

where $\tau$ is the averaging time, $N$ is the total number of samples and $m$ is the averaging factor, $y_i$ is the $i$th sample of emission time delay in time series as shown is figure 6(a).

To calculate the Allan deviation, the HHG signals with both jets on were measured continuously at 100 ms intervals at

---

**Figure 3.** Images of (a) Gyger micro valve, (b) needle jet located in mount (top view), (c) needle jet located in mount (side view), (d) gas jet connected to two micro valves attached with the solenoid coil. (e) Gouy phase interferometer inside the HHG generation chamber. The electrical connections for triggering the micro valves (blue wires) and gas lines (white tube) are connected into the chamber by feedthrough connections.
a particular gas jet separation (where both jets had similar HHG intensity). We also measured HHG signals with individual gas jets turned on separately. Then from the normalized intensity data the Gouy phase shift can be obtained. The experimental phase shift is then converted to emission time delay as $t_{Gouy}$. Details of the data normalization procedure are presented in section 4.1. As shown in figure 6(b) the best timing resolution is $\sim 160$ zs and for measurement times between 10 and 50 s resolutions is $< 200$ zs. Taking this into account the typical data acquisition time was kept at 15 s.

4.1. Temporal coherence measurement

To observe the temporal coherence, normalized HHG intensity for several harmonic orders as a function of separation between the two gas jets was determined as

$$I_N = \frac{I_{12}}{I_1 + I_2 + 2\sqrt{I_1 I_2} \cos(\phi_{Gouy})},$$

(7)

where $I_{12} = I_1 + I_2 + 2\sqrt{I_1 I_2} \cos(\phi_{Gouy})$ is the coherent sum of the intensities when both jets are simultaneously on and $I_1, I_2$ are the intensities either from top or bottom jet respectively.

4.1.1. Argon measurements. Argon was used as the first atomic gas species to test the interferometer. The temporal coherence of the HHG signal was measured while the gas jets separation was varied. The normalized intensity for a range of harmonic orders from $H_{23}$ to $H_{35}$ is shown in figure 7(a) as a function of gas jet separation. When separation between the jets is zero, HHG emissions generated from the two gas jets constructively interfere. As the gas jets separation increases the HHG radiation emitted by the moveable jet undergoes a phase shift in respect to the fixed jet. It is clearly observed that each harmonic exhibits both constructive and destructive interferences as the separation between the jets is varied. It was previously demonstrated that the observed fringes are mainly a result of the Gouy phase shift of the generating IR laser pulses being imparted on HHG emissions generated in the translated gas jet [15]. While it is expected that the fringe visibility be 100% if the two XUV pulses are perfectly coherent, this is not the case in our measurement due to a less than perfect overlap of the two HHG signals in the far field.

The normalized intensity as a function of trigger delay between laser pulse and micro valve opening at three different valve opening times.

Figure 4. (a) Schematic of devices combination that allow single laser shot HHG signal readout. Micro valve and camera are triggered with corresponding input laser pulse. Trigger delay is given by the user through LabVIEW code. MVC 1 controls the working condition of the micro valves. Each CMOS output frame is transfer through camera link cable and frame grabber allow high speed digital imaging. (b) 40 MHz FPGA clock is employed for the timing of micro valves and CMOS camera triggering. Trigger delays are synchronized with the laser pulse by a LabVIEW program. The timing jitter of the 40 MHz FPGA clock is 25 ns at most and does not affect the HHG condition as the FPGA clock is synchronous with 1 kHz repetition rate laser pulse. (c) HHG yield as a function of trigger delay between laser pulse and micro valve opening at three different valve opening times.
can be rewritten as
\[
\frac{1}{z_c} = \frac{1}{2\pi} \left[ q \frac{d\phi_{\text{Gouy}}}{dz} + d\psi_S \right]
\]

Figure 7(d) shows the plot of inverse of the coherence distance \(1/z_c\) versus the harmonic order \(q\). The red line is the fit of equation (8) that is the derivative of the Gouy phase and the combined effect due to electron travel time and the action term, whereas the blue line indicates the revival distance when only the Gouy phase is considered. The retrieved Rayleigh length of the driving laser pulse from the experimental data is 13.6 ± 1.7 mm and the estimated Rayleigh length from beam profiling measurement is 14.4 ± 1.4 mm. The agreement with the Rayleigh length...
measurement supports the conclusion that the phase shift between two XUV emissions occurs mainly due to the Gouy phase variation of the driving laser. The action derivative term estimated from the $y$ intercept of the fitted line is $-132 \pm 34 \text{ rad m}^{-1}$. This term mainly comes from the difference in semi-classical action of the returning electron during its travel in the electric field.

4.1.2. $H_2$ measurement. Generally the ionization and recombination processes of HHG in molecules are interesting and more complex than atomic systems due to the additional degrees of freedom in their nuclear motion. In fact, the motivation for building this advanced Gouy-phase interferometer is to extract the relative phase of harmonics from molecular isotopes as a means for extracting their nuclear dynamics. However, in comparison to Ar obtaining a high-yield HHG signal from $H_2$ is more challenging. This is because the compression ratio of turbo molecular pump decreases exponentially with lighter molecule [22]. The compression ratio of lightest $H_2$ molecule decrease by $\sim 130$ times compared to Ar so it is harder to pump [23]. In particular, it is important to maintain the background pressure less than $1 \times 10^{-6}$ Torr to avoid MCP damage. Due the pulsed micro valves and synchronized to laser pulses we can increase gas density in the interaction region while keeping the background pressure low in order to get sufficiently strong HHG signal from $H_2$. Figure 8(a) shows the normalized HHG signal for $H_2$ from harmonic order $H_{23}$ to $H_{35}$. The retrieved Rayleigh length of the driving laser from the fitted line of figure 8(d) is $16.7 \pm 1.6$ mm and the measured Rayleigh length estimated from the beam profile is $14.4 \pm 1.4$ mm. The action derivative term is $-67.6 \pm 29.7 \text{ rad m}^{-1}$ from the $y$ intercept of the fitted line.

Thus, we performed temporal coherence measurements for HHG emissions from Ar and $H_2$ using the advanced Gouy-phase interferometer. The retrieval of Rayleigh length in agreement with beam profiling indicates that the phase shift between the two XUV pulses generated by two gas jet situated at different places within the laser focus is due to
the temporal delay in electron recombination caused by the Gouy phase shift of the driving laser and are independent of the HHG generating medium.

5. Conclusions

The design, characterization and optimization of an XUV Gouy-phase interferometer have been presented. This approach, utilizing dual gas jet sources placed simultaneously within a single laser focus avoids the complexity of using additional optical components for splitting the fundamental laser beam as well as added complexity of the HHG detection system. The inherent stability, data normalization and short acquisition time greatly reduce the random and systematic uncertainties arising from various fluctuations and instabilities in the driving laser pulses, gas densities and mechanical elements of an interferometer. The use of pulsed micro valves, synchronized with the laser pulses ensures sufficiently high gas density in the interaction with low background pressure, enabling us to obtain very clean HHG spectra from hydrogen molecules. The interferometer could be further improved by use of XUV spectrometer with lower XUV loss. The coherence measurements have been performed on HHG radiation generated by both atomic and molecular gases. The interferometer is capable of measuring a phase shift of XUV radiation on the order of milli-radians corresponding to sub-attosecond time resolution in emission delay measurements. Due to its high stability and resolution the interferometer can prove to be a useful tool for studying ultrafast phenomena in atomic and molecular physics. The most obvious future application of the Gouy-phase interferometer is a precise measurement of a phase shift in XUV emissions from hydrogen isotopes in order to study their ultrafast dynamics during HHG process [24, 25].

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