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Transport of hydrogen radicals in a hydrogen plasma jet and an experimental setup to monitor molecular hydrogen

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Transport of hydrogen radicals in a hydrogen plasma jet and an experimental setup to monitor molecular hydrogen

P.J.W. Vankan

5th October 2000
SUMMARY

Plasma expansion is of importance in several physical subjects, like surface modification (thin film deposition, etching, passivation), nuclear fusion and astrophysics. In those fields atomic hydrogen radicals play an important role. In this graduation work the transport mechanisms of ground state hydrogen atoms in a hydrogen plasma expansion have been investigated by means of the Two-photon Absorption Laser Induced Fluorescence technique.

In the case of an expanding thermal plasma generated from molecular hydrogen, it has been discovered that the jet main constituent is \( \text{H}_2 \), \( \text{H} \) atoms being in the minority. It has been shown that the atomic hydrogen forward flux in the core of the plasma jet is not conserved. For instance throughout the stationary shock wave the velocity decreases, the density however does not increase as expected from gas dynamics. \( \text{H} \) atoms do not recombine in volume but escape the jet by diffusion. This diffusion process is driven by large \( \text{H} \) atom density gradients between the core of the plasma jet and its surroundings. These gradients exist due to the loss of \( \text{H} \) atoms at the wall where they recombine to form \( \text{H}_2 \). The influence of the mass on the outward diffusion of hydrogen has been investigated by seeding the jet with deuterium. It was found that radicals with a higher mass were better confined. Increasing the background pressure also leads to a better confinement. This confirms the picture of \( \text{H} \) atoms escaping the plasma jet by a diffusion process.

It has been shown that the \( \text{H} \) atom velocity distribution function in the stationary shock wave is not Maxwellian, i.e. the flow is not in equilibrium. The measured distribution function could be well approximated by two separate Maxwellian terms belonging to the supersonic and subsonic parts of the flow. It has been proven that molecules can enter the plasma jet. For that deuterium molecules have been seeded in the background gas and the created deuterium atoms have been monitored inside the plasma jet. Already in the shock region the deuterium molecules were able to enter the jet and react to form \( \text{D} \) atoms.

In order to get a complete overview of the jet transport properties, the hydrogen molecules have to be probed. The re-entry of molecules into the plasma jet is also an important issue. It plays a role in the shock formation but it is also of importance for the mixing with the ambient gas, e.g. the mixing of the precursors with the jet particles in plasma assisted chemistry. To be able to unambiguously proof that molecules re-enter the plasma jet one has to monitor the deuterium and hydrogen molecules. In the wall recombination of atomic hydrogen \( \text{H}_2 \) molecules are believed to be formed rovibrationally excited. The \( \text{H}_2(r, v) \) plays an important role for example in the production of \( \text{H}^- \). To better understand the wall recombination process one has to measure the vibrational population distribution of ground state \( \text{H}_2 \).

Three detection schemes for hydrogen molecules have been proposed. For these schemes UV or vacuum UV photons are needed. These vacuum UV photons can be generated by Stimulated Anti-Stokes Raman Scattering using a Raman cell. This process has been tested and it was shown that it can be used to generate the vacuum UV photons. A setup has been designed to detect molecular hydrogen in all the vibrational states.
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Since radicals are very reactive particles they play a key role in many chemical processes. Also in the chemistry of plasmas radicals initiate all kind of reactions. For example in the deposition of hydrogenated amorphous silicon (a-Si:H) for the next generation thin film solar cells atomic hydrogen radicals are needed to produce SiH₃ radicals which are the main contributor in the deposition process. Therefore in this specific case the radical generation, transport and recombination needs to be known to better understand the growth mechanisms and the related film properties.

One of the limiting factors in the growth of a-Si:H is the transport of the radicals to the substrate. Now a low growth rate results in high production costs. Nowadays new techniques are used to improve the transport of the particles to the substrate. A possibility is to use expanding thermal plasmas. In the beginning of the plasma expansion the H atoms react with SiH₄ to form SiH₃ radicals and the radicals are then transported downstream to the substrate. An efficient transport of the created radicals is therefore necessary for high growth rates. The transport of radicals is however highly influenced by their reactivity. Since hydrogen is the initiator of the process and is also needed in the actual deposition a study of the H atom transport is well grounded.

Recently it is believed that the reactor walls of Tokamaks have a large impact on the edges and stability of the plasma. This is mainly due to the processes that take place at the surfaces. One of these processes is the surface recombination of radicals forming molecules. Hydrogen atoms for example recombine at surfaces forming hydrogen molecules, which are believed to be rovibrationally excited. The surface recombination influences the transport of particles in Tokamak plasmas but also in expanding plasmas used for fast deposition of thin layers. Surface recombination also influences the plasma chemistry through the formation of molecules, especially when they are excited. For example rovibrationally excited hydrogen molecules are important in fusion plasmas for the generation of H⁻.

In the group Equilibrium and Transport in Plasmas (ETP) in Eindhoven a plasma source has been developed that can handle high gas flows to obtain high deposition rates. The plasma source parameters can all be varied, including the position of the plasma inside the vessel. It is also possible to insert a substrate into the plasma. All kind of parameters like substrate material, temperature and position can be changed. In Eindhoven a wide variety of diagnostic techniques is available, including a technique to monitor atomic radicals. A new technique to monitor ground state hydrogen molecules is being developed. For these reasons the experimental arrangement is very well suited to study both the transport and the surface recombination of radicals.
Part I

ATOMS
Chapter 1

INTRODUCTION

This report is the result of a graduation project in the group Equilibrium and Transport in Plasmas at the Eindhoven University of Technology. The project has been performed in the field of non-linear laser spectroscopy applied to the diagnostics of low temperature plasmas.

Plasma expansion is a very general physical phenomenon being of interest in a very broad range of physical subjects. The dimensions range from large scale astrophysical objects [1] to medium scale nuclear fusion [2] and small scale laser spots [3]. The transport of atomic radicals in particular plays a key role in the chemistry and transport properties of plasma expansions. Knowledge about this is therefore needed to improve applications like depositions of thin films, e.g., solar cells [4, 5, 6], and like surface modification [7]. Hydrogen plasmas are of particular importance since it is the most abundant form of matter in the universe, because in nuclear fusion hydrogen plasma are being used and because hydrogen plays a fundamental role in the chemistry of deposition plasmas.

In the first part of this report the transport mechanisms of ground state hydrogen atoms in a pure hydrogen plasma will be described in detail. The transport of atomic hydrogen in an Ar-H$_2$ plasma has been reported earlier [8]. The H atoms exhibit an anomalous expansion pattern. They are able to escape the core of the plasma jet. This so-called radical defocussing effect is shown to be a direct consequence of plasma wall interactions. The hydrogen atoms have been probed via Two-photon Absorption Laser Induced Fluorescence (TALIF) resulting in spatially resolved densities, temperatures, velocities and velocity distributions.

In this part first a brief introduction of the theory of plasma expansion and the TALIF technique will be given. Then the experimental setup will be shortly described. The results on the transport properties of H atoms will be given and discussed. The influence of the mass on the transport of radicals will is studies by adding some deuterium molecules in the background and probing the deuterium atoms. The reentry of deuterium molecules into the plasma jet and its influence on the shock formation process will be discussed. Finally some conclusions will be drawn.
Chapter 2

THEORY

This chapter will treat the theoretical aspects of the TALIF technique and the plasma expansion. Two-photon Absorption Laser Induced Fluorescence (TALIF) will be briefly explained together with the quantities one can obtain using this technique. Then the expansion structure of the plasma jet will be discussed.

2.1 Two-photon Absorption Laser Induced Fluorescence

Two-photon Absorption Laser Induced Fluorescence (TALIF) is nowadays a well established technique to measure groundstate atoms, [9, 10, 11]. This technique uses two UV photons to excite the atoms instead of one vacuum UV photon. In the experiments reported of here the TALIF method has been used to probe hydrogen atoms. The detection scheme is shown in figure 2.1. Two 205 nm photons are used to excite H to the n=3 state, and the fluorescence back to the n=2, the Balmer-α light, is detected [11].

Using this technique several quantities can be measured. In figure 2.2 these quantities are depicted. The measured signal intensity as a function of frequency is usually of Gaussian shape. This indicates that the probed particles, i.e. the plasma heavy particles, have a Maxwellian velocity distribution. This so called Doppler broadening of the peaks is mainly caused by the thermal motion of the H atoms. The width of this peak is then determined by the temperature via the following formula [12].

\[ T = \frac{m_H c^2}{8 \ln 2 k} \left( \frac{\delta \nu}{\nu} \right)^2 \]  

(2.1)

where \( m_H \) is the hydrogen atom mass, \( k \) is the Boltzmann constant, \( c \) is the speed of light, \( \nu \) is the frequency of the transition and \( \delta \nu \) is the FWHM value of the profile. Since the line profile is the convolution of the laser profile and the Doppler broadened profile the laser profile has to be taken into account. This can be done by using a Voigt function, which is the convolution of a Gaussian and a Lorentzian peak, or by using a Gaussian as the sum of the Gaussian from the Doppler broadening and a Gaussian from the laser profile.

The area under the curve is proportional to the density \( n \). The densities are however only relative and need to be calibrated. The calibration procedure is extensively described in chapter 4.1.
From the Doppler shift of the peak the H atom velocity \( v \) in the direction of the laserbeam can be calculated.

\[
v = \frac{\Delta \nu}{\nu_{\text{th}}}
\]

(2.2)

where \( \Delta \nu \) is the Doppler shift, and \( \nu_{\text{th}} \) is the theoretical value of the transition.

### 2.2 Free jet expansion

The expansion of a plasma is comparable with the expansion of a neutral gas [13, 14]. The typical structure of a neutral gas expansion from a high pressure reservoir into a low pressure vacuum chamber is depicted in figure 2.3. Several regions can be distinguished depending on the Mach number. The Mach number \( M \) is given by

\[
M = \frac{v}{c_s},
\]

(2.3)

\[
c_s = \sqrt{\frac{\gamma k T}{m}}
\]

(2.4)

where \( v \) is the gas velocity, \( c_s \) is the local speed of sound, \( \gamma \) is the isentropic coefficient, \( k \) is the Boltzmann constant, \( T \) the local temperature and \( m \) the mass of the gas. The gas exits the reservoir at sonic speed \( (M = 1) \) and accelerates into the supersonic regime of the expansion. The density and the temperature decrease rapidly and the velocity increases quickly. The density decrease, also called rarefaction, is due to the increase in the jet diameter during the expansion process. The temperature decrease and velocity increase is due to conversion of
thermal energy into directed motion. At some distance from the source particles from the jet collide with the residual background gas. This leads to the formation of a stationary shock wave across which the flow undergoes a transition from a supersonic regime to a subsonic regime. The velocity decreases and the temperature starts to increases due to conversion of directed motion into thermal energy by collisions. The density increases since the forward flux is conserved and the expansion radius stays constant throughout the stationary shock wave. Behind the Mach disk ($M = 1$) the gas expands subsonically. The shock wave thickness, e.g. the distance from beginning of the shock to Mach disk is always in the order of a few mean free paths for momentum exchange. In radial direction the expansion is limited by the barrel shock. This behavior of the density, temperature and velocity in the along the jet centerline is shown in figure 2.4.

The plasma expansion can now be described using this supersonic free jet theory for neutral gas. Since the particles in first order originate from a point source and flow along straight flow lines the density in the supersonic regime along the jet centerline is given by the following formula

$$n(z) = n_0 \frac{z_{ref}^2}{(z + z_{source})^2}$$  \hspace{1cm} (2.5)

where $n_0$ is the density in the source , $z_{ref}$ is a scaling length determined by the source nozzle geometry, and $z_{source}$ is the location of the virtual point source. In case of a neutral gas expansion the energy equation can be replaced by the Poisson equation since the supersonic expansion is isentropic.

$$\left( \frac{n}{n_0} \right)^{\gamma-1} = \frac{T}{T_0}$$ \hspace{1cm} (2.6)

where $\gamma$ is the isentropic coefficient, which is $\frac{5}{3}$ for a monoatomic gas, and $T_0$ is the source temperature. Since the temperature is a measure for the spread in velocity the temperature
in a supersonic expansion is often split into a temperature parallel and perpendicular to a stream line in the flow. It has been experimentally shown that neutrals and charged particles follow the gas expansion laws, with a smaller isentropic coefficient [15]. Radicals, i.e. very reactive particles like H and N, have a deviant expansion. The radicals escape the core of the plasma jet by a diffusion process induced by recombination of H atoms at the vessel walls [8]. Therefore the density decrease along the jet centerline is faster for radicals than for neutrals. On the jet centerline the radical density can be expressed by the following formula

\[
 n(z) = n_0 \left( \frac{z_{ref}}{z + z_{source}} \right)^\beta
\]  

(2.7)

with \( \beta \) the so called expansion coefficient; \( \beta > 2 \) since the diffusion loss is added to the classical rarefaction loss.

At the end of the supersonic expansion a stationary shock wave is formed. In the shock region the plasma particles collide with the background particles. Therefore the velocity of the expansion particles decreases and the temperature increases. Since the forward flux is conserved the density increases abruptly in the shock. The Rankine Hugoniot relations connect the jump in temperature and density to the Mach number in front of the shock,

\[
 \frac{n_2}{n_1} = \frac{v_1}{v_2} = \frac{(\gamma + 1)M_1^2}{(\gamma - 1)M_1^2 + 2}
\]  

(2.8)

\[
 \frac{T_2}{T_1} = \frac{[2\gamma M_1^2 - (\gamma - 1)] [(\gamma - 1)M_1^2 + 2]}{(\gamma + 1)^2 M_1^2}
\]  

(2.9)

The location of the Mach disk \( z_M \), the end of the shock where the Mach number \( M \) equals 1, is given by the following formula [13]
\[ z_M^2 = 2.5 \Phi \frac{1 + \frac{\gamma_0}{2} \sqrt{T_0 A}}{\sqrt{\gamma_0} P_{\text{back}}} \quad \text{derived from (2.10)} \]

\[ z_M = 0.7 d \sqrt{\frac{P_{\text{stag}}}{P_{\text{back}}}} \quad \text{(2.11)} \]

where \( \Phi \) is the heavy particle flow in standard \( m^3 s^{-1} \), \( \gamma_0 \) is the isentropic coefficient in the reservoir, \( A \) is the atomic mass number, \( T_0 \) is the source temperature in K and \( P_{\text{back}} \) is the background pressure in the vessel in Pa. In equation 2.11 \( d \) is the arc channel diameter and \( P_{\text{stag}} \) is the stagnation pressure inside the arc channel. In the subsonic domain the plasma flows at constant pressure.
Chapter 3

EXPERIMENTAL SETUP

A simplified scheme of the experimental set up is depicted in figure 3.1. For the experiments reported in this paper the cascaded arc plasma source has been modified to operate with a pure hydrogen plasma. The diameter of the arc channel is 4 mm and the length of the arc is 4 plates. The operating conditions of the arc are a dc current of 55 A and a cathode-anode voltage of 150 V and a gas flow of 3.5 slm H₂, giving a stagnation pressure of 0.14 bar. The generated plasma expands from a straight nozzle into a roots-blower pumped vessel. The background pressure can be varied from 10 Pa to 1 atm. The cascaded arc plasma source is mounted on a translation arm. Spatial scans through the expanding plasma can be made by moving the arc relative to the intersection of laser beam and detection volume.

A tuneable dye laser (Quanta-ray PDL-3) is pumped with the second harmonic (532 nm) output beam of an injection seeded pulsed Nd:YAG laser (Quanta-ray GCR-230) operating at 20 Hz. The dye laser delivers radiation around 615 nm (sulforhodamine 640) with a pulse energy of 100 mJ and a pulse duration of 6 ns. The dye laser output is then frequency doubled using a KDP crystal. Upon exiting the KDP crystal the polarisation of the generated blue beam is rotated to coincide with the polarisation of the red beam. Both collinear laser beams are aligned through a BBO crystal where a sum-frequency process leads to the generation
of an UV laser beam around 205 nm with an energy per pulse up to 2 mJ. Both crystals are electronically angle tuned by means of a feedback system to provide a constant output energy when scanning the dye laser. The UV laser beam is horizontally polarised and its frequency profile is approximately Gaussian with a bandwidth of 0.25 cm\(^{-1}\) as measured by a two-photon excitation process on atomic N at room temperature.

The UV laser beam is directed towards the vacuum chamber using a set of high reflectivity dielectric mirrors centered at 205 nm. Those mirrors are also used to remove the residual blue and red laser beams which are dumped. The TALIF probe beam (\(d = 2\) mm) is then directed perpendicularly to the plasma jet axis. It is tightly focused (\(w \approx 10\) \(\mu\)m) by a MgF\(_2\) lens (\(f = 600\) mm) through a quartz window into the vessel. The focus is centered on the plasma beam axis. The excited state fluorescence yield originating from the focus is imaged perpendicularly to the laser probe beam by means of two plano-convex lenses onto an adjustable 2-dimensional slitmask, which defines the spatial resolution, located in front of a gated photomultiplier tube (PMT) (Hamamatsu R928). The continuous background light emitted by the plasma is strongly reduced by a 10 nm FWHM interference filter centered at 656 nm. The signal from the PMT is fed directly to the input of an oscilloscope which is connected to a computer used for data acquisition and to control the laser system.
Chapter 4

RESULTS AND DISCUSSION

This chapter is about the results of the TALIF experiment on an expanding hydrogen plasma. First the calibration of the density using krypton will be shown. Then the transport along the jet centerline will be discussed in terms of density, temperature and velocity. The radial profile will be presented and finally the influence of mass on the transport and the re-entry of molecules into the jet will be discussed.

4.1 Density calibration using krypton

Since the densities measured via LIF are relative, the measurement has to be calibrated. In order to do this the fluorescence has to be related to a known amount of atomic hydrogen or to a known amount of another gas of which the cross section ratio with H is known. To obtain a known amount of atomic hydrogen is very difficult [16]. Therefore the calibration has been performed using krypton. The ratio of the two-photon cross sections of krypton to hydrogen has been recently measured [17] to be 0.62.

The krypton detection scheme is shown in figure 4.1. Krypton is excited by two 204.2 nm photons to an excited state and this state radiates at 826 nm to a lower state. The transition is very easily saturated. In order to be sure that the calibration was done in the non-saturated regime the fluorescence has been measured as a function of the laser energy. The results are shown in figure 4.2. At energies below 0.18 mJ the transition is not saturated since the slope is approximately 2, i.e. the fluorescence is a quadratic function of the laser energy. At higher energies the slope decreases to 1.6. There the transition starts to be saturated. The measurements have been performed at energies around 0.12 mJ.

In the unsaturated regime the groundstate atomic hydrogen density can be calculated from the krypton density by

\[ n_H = n_{K^*} \frac{S}{S_{K^*}} \frac{\sigma_{K^*}^{(2)}}{\sigma_H^{(2)}} \left( \frac{\nu_H I_{K^*}}{\nu_{K^*} I_H} \right)^2 \frac{A_{K^*} \tau_{K^*} T_{K^*}}{A_H \tau_H T_H} \frac{\epsilon_{K^*} G_{K^*}}{\epsilon_H G_H} \]  \hspace{1cm} (4.1)

where \( n \) is the density, \( S \) is the total fluorescence, and \( \sigma^{(2)} \) is the two-photon cross section. \( \nu \) is the transition frequency, \( I \) is the laser power, \( A \) the transition probability and \( \tau \) the lifetime. \( T \) is the optical transmission of the detection branch, \( \epsilon \) is the quantum efficiency and \( G \) the gain of the PMT. The used values for these parameter have been listed in table 4.1. Identical
Fig. 4.1: The detection scheme of krypton atoms

Fig. 4.2: The krypton fluorescence as a function of the laser energy. Around 0.18 mJ the krypton transition starts to saturate. Note that both the axis are logarithmic

laser beam geometry and profile have been assumed. A longpass filter, transmittance 0.95 above 700 nm, has been used to reduce the stray light.

The lifetime of the excited H state $\tau_H$ has been taken to be 10 ns instead of the theoretical 15 ns [18]. This decrease arises from $\ell$-mixing of the $n=3$ levels by the laser beam electric field. This has been verified by measuring the time resolved LIF signal using a fast PMT (Hamamatsu H5783P). The lifetime has been measured at several axial positions in the jet. No change in $\tau$ has been observed however. An example of the TALIF signal can be found in figure 4.3.

The krypton profiles have been taken at room temperature and at a pressure of 10 Pa corresponding to $2.44 \cdot 10^{21}$ m$^{-3}$. An example is shown in figure 4.4. The profile is a convolution of the Doppler-broadened krypton line and the laser spectral profile. The asymmetry in the measured profile arises from the laser profile. The Doppler width of the krypton line is 0.13 cm$^{-1}$.

A Voigt profile, the convolution of a Gaussian and a Lorentzian profile, has been fitted to

<table>
<thead>
<tr>
<th>$I_{laser}$ in mJ</th>
<th>krypton</th>
<th>hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$ in s$^{-1}$</td>
<td>$3.5 \cdot 10^7$</td>
<td>$4.4 \cdot 10^7$</td>
</tr>
<tr>
<td>$\tau$ in ns</td>
<td>26.9</td>
<td>10</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>0.015</td>
<td>0.07</td>
</tr>
<tr>
<td>$T$</td>
<td>0.95</td>
<td>1</td>
</tr>
<tr>
<td>$G$</td>
<td>$5 \cdot 10^6$</td>
<td>$5 \cdot 10^6$</td>
</tr>
</tbody>
</table>

Tab. 4.1: The values of all the parameters used in the calibration with krypton.
the krypton line resulting in a linewidth of $0.35 \text{ cm}^{-1}$ at 205 nm for the laser. This value is slightly higher than the value measured using Nitrogen atoms. This is probably due to a misalignment of the dye laser.

4.2 Transport of H atoms along the jet centerline

4.2.1 Density and perpendicular temperature

The axial H atom density profile has been plotted in figure 4.5. In the supersonic part of the expansion the expected density decrease can be seen. At 20 Pa the density profile does not exhibit a jump throughout the stationary shock wave but a plateau like structure, whereas the drift velocity decreases and the temperature increases. At 100 Pa the density profile does show a jump of approximately 1.4 in amplitude. The Mach number in front of the shock has been measured as will be reported in section 4.2.2. It can be determined from the H atom velocity and the speed of sound at the beginning of the shock. Using the Rankine-Hugoniot relation equation 2.8 the theoretical density jump can then be calculated. The Mach numbers are equal to 3.9 at 20 Pa and 2.8 at 100 Pa. This should give a density jump of 3.7 at 20 Pa whereas there is no increase at all. At 100 Pa the density jump should be 2.9, which is much bigger than the measured 1.4.

This absence of a density jump leads to a non-conservation of the forward H flux as reported in an Ar-H$_2$ expansion by Mazouffre et.al. [8, 19]. The background density of H atoms is very low due to the surface recombination of hydrogen atoms forming H$_2$ molecules. This low background density gives rise to large density gradients between the ambient gas and the core of the jet causing H to diffuse out. It has been shown that the particle densities are too low to lead to any significant loss of H radicals by volume recombination.

The density decay in the supersonic part at 20 Pa can be fit by equation 2.7. The expansion coefficient $\beta$ equals 2.7 meaning that the decay is faster than a normal adiabatic expansion.
Fig. 4.5: The H atom axial density profile at two background pressures. At 20 Pa there is no density jump across the stationary shock wave, meaning that the forward H flux is not conserved. At 100 Pa there is a density jump, but its amplitude is too small.

Fig. 4.6: The H atom axial perpendicular temperature profile at two different background pressures. First the temperature decreases since thermal energy is converted into directed motion. Then the particles collide with the background and the temperature will increase due to the conversion of the directed motion into random thermal motion by collisions. In the subsonic part the temperature decreases gradually due to heat transfer to the vessel walls.
This is also explained by the outward diffusion of H atoms superimposed upon the normal rarefaction effect. This directly means that the barrel shock, the shock structure at the side of the expansion, is permeable for the radicals in the expansion. The source density also follows from equation 2.7, \( n_0 = 3 \cdot 10^{22} \text{ m}^{-3} \).

Equation 2.7 also gives information on the expansion geometry. This is different than expected using a straight nozzle. Using a fixed value for \( z_{\text{ref}} \) of one nozzle radius, 2 mm, \( z_{\text{source}} \) was found to be -5 mm. This means that the expansion already starts inside the nozzle. When using a straight nozzle the expansion is however expected to start a few millimeter after the nozzle. This could be explained by the loss of H atoms inside the nozzle by diffusion to the nozzle wall due to gradients induced by wall recombination. This gives rise to a density decay already before the start of the expansion.

The perpendicular temperature profile along the jet axis is plotted in figure 4.6 for two background pressures. The temperature drops quickly in the supersonic region. This drop, expressed by equation 2.6, is due to the conversion of thermal energy into directed motion. The temperature reveals a clear shock structure where the directed motion is converted back into thermal energy due to the collisions with the background gas. The shock location and shock thickness depend very clearly on the background pressure. In the subsonic part of the expansion the temperature decreases due to heat transfer to the vessel walls.

The location of the beginning of the shock and the Mach disk has been determined from the temperature and density profiles. The velocity profile will be looked at in the next chapter. For 100 Pa the shock wave starts at 6 mm from the nozzle and the Mach disk is located at 14 mm determined from the temperature. These limits fit with the density profile. At 20 Pa the beginning of the shock is located at 10 mm and the Mach disk is located around 35 mm determined from the temperature. For the density these limits are not so clear. In figure 4.7...
the axial density profile is plotted until 20 mm. The supersonic expansion part (until 10 mm) has been fitted using equation 2.7. The densities are clearly higher after than expected from the expansion fit. This reveals that the shock already starts at 10 mm. It is not very evident however because of the large outward diffusion of the H atoms in the beginning of the shock. The large outward diffusion of the H atoms can be explained by the large mean free paths. In the shock the H atoms mainly collide with H₂, the main constituent of the background gas. The mean free path can then be calculated by

\[ \lambda_{H-H_2}^{mf} = \frac{1}{n_{H_2} \sigma_{H-H_2}} \]  (4.2)

\( n_{H_2} \) has been measured previously using Coherent Anti-Stokes Raman Scattering by Meulienbroeks [20]. These measurements were however on a different plasma and the spatial resolution was poor (1 cm). \( \sigma_{H-H_2} \) has been calculated by Phelps [21] to be \( 10^{-19} \, \text{m}^{-2} \) at 500 K. With a value of \( 2.10^{21} \, \text{m}^{-3} \) for \( n_{H_2} \) follows a mean free path of approximately 5 mm near the Mach disk at 20 Pa. The mean free path in the beginning of the shock is than even higher since the H₂ density will be a factor of around 3 or 4 smaller. The mean free path there would then be in the order of 15 mm. The shock thickness at 20 Pa is 30 mm thus roughly in the order of two times the mean free path. \( \lambda_{H-H_2}^{mf} \) is then in the order of the jet dimension enabling H atoms to diffuse out of the core of the jet. The flow can not be completely described by the hydrodynamic theory any more and one has to go to gas kinetics calculations.

The isentropic coefficient \( \gamma \) and the source temperature \( T_0 \) can be determined from the temperature as a function of the density in the supersonic regime, see figure 4.8 and using equation 2.6. At 20 Pa \( \gamma = 1.55 \pm 0.05 \) meaning that the expansion is non-adiabatic. At 100 Pa the error on \( \gamma \) is very large (0.3) but the expansion is close to adiabatic so \( \gamma \approx \frac{5}{3} \). The non-adiabaticity at 20 Pa can be explained by heat transfer from both the source and the hot background gas. It could also be explained by H₂ re-entering the plasma jet disturbing the temperature profile. At 20 Pa the source temperature equals \( 5000 \pm 3000 \) K or 0.45 eV. This is however very dependent on the form of the expansion, equation 2.7.

Using equation 2.10 now the Mach disk location can be calculated. At 20 Pa the Mach disk is located at 35 mm, determined from figures 4.5 and 4.12, compared to a calculated value of 33 mm. In this calculation the mass number has been taken as 2. The discrepancy is due to the uncertainty of the measurement of the Mach disk location. At 100 Pa the measured value is 14 mm and the calculation gives \( z_M = 15 \) mm.

### 4.2.2 Axial velocity and parallel temperature

The velocity is determined from the Doppler shift of the transition. In the supersonic and subsonic regions of the expansion the line profile is Gaussian implying a Maxwellian velocity distribution. Throughout the shockwave however the line profile is not Gaussian any more as can be seen in figure 4.9. This implies a non equilibrium situation for the flow.

In a first order approximation the non-Gaussian line profiles can be composed of the sum of two separate Gaussians. They represent a velocity distribution consisting of the sum of two separate Maxwellian terms with velocities and temperatures corresponding to the supersonic
Fig. 4.9: Eight frequency profiles at 20 Pa starting ahead of the shock and ending behind the shock have been plotted. It is clear that the H atoms distribution function inside the shock region is not Maxwellian. The profiles have been fitted using two separate Maxwellian velocity distributions.
Fig. 4.10: The densities of the supersonic (square) and subsonic (circle) parts of the flow. The total density is plotted with open triangles. At the left hand side the background pressure is 20 Pa, and at the right hand side the pressure is 100 Pa. Throughout the stationary shock wave the supersonic part loses density to the subsonic part.

and subsonic flows. Starting with one distribution in the supersonic region the particles start to collide with H₂, the background particles, i.e. they start to shock. Then a second distribution of subsonic particles appears. Moving along the shock particles change from the supersonic distribution to the subsonic distribution. At the end of the shock all the particles have changed from the initial distribution to the subsonic distribution. This view is confirmed by figure 4.10 were the densities of the supersonic and subsonic parts of the flow are plotted throughout the stationary shock wave. The velocity profile has already been predicted for a rarefied expansion in 1951 by Mott-Smith [22]. Mott-Smith also predicted the density profile. But he did not account for the outward diffusion of H atoms. Therefore the density can not be described using the Mott-Smith model.

In figure 4.11 both the temperature and velocity of the supersonic and subsonic components of the distribution have been plotted together with the averaged ones for two background pressures. The supersonic component of the distribution starts to collide with the background particles. When a particle has collided it changes to the subsonic component. The supersonic component does not contain particles that have already collided and will therefore show the temperature decreasing as expected in a normal expansion. At the end of the shock all the particles have moved from the supersonic to the subsonic component, see 4.10. Since most particles are H₂ molecules the collisions are mainly H-H₂ collisions. From the H atom velocity jump of the supersonic to the subsonic component, which is roughly three in the beginning, then increases a little and near the Machdisk decreases again, one can derive information about the particles the H atoms collides with. A possibility is that one collides with H₂ molecules entering the jet from the side. This could be possible since the mean free path is in the order of the barrel shock dimension enabling the hydrogen molecules to enter through the barrel shock without colliding. This however needs to be better studied.

In order to analyze the data it is then necessary to determine the first moment of the distribution. In a normal Maxwellian distribution the equals the mean velocity. In case of a two velocity distribution it is equal to the density averaged velocity. An axial profile of the first moment of the distribution, for convenience further referred to as the velocity, at a background
Fig. 4.11: The temperature and velocity of the two distribution components, and the averaged temperature and velocity at background pressure of 20 Pa (upper two) and 100 Pa (lower two). The averaged one is depicted by an open triangle, the supersonic component by a filled square and the subsonic component by a filled circle.

Pressure of 20 Pa has been plotted in figure 4.12. The line gives the local sound speed. The sound velocity has been determined from the parallel temperature taking an effective mass of $m = 1.5$ amu for the H/H$_2$ mixture. The average temperature has been defined as the density averaged temperature. This temperature is the one that light particles like electrons will feel. The velocity increases to 7500 m/s at 10 mm. After 10 mm the velocity starts to decrease. The stationary shock wave thus starts at 10 mm in agreement with the density and temperature profiles. At 100 Pa the average velocity has been plotted in figure 4.13. The expansion shocks earlier and the expansion can expand less than in the 20 Pa case. The highest velocity is 6250 m/s. The shock starts approximately at 6 mm, in agreement with the perpendicular temperature and density profiles. The maximum velocity that can be reached in an expansion is

$$v_{max} = \sqrt{\frac{2\gamma kT_0}{\gamma - 1} m_{eff}}$$

(4.3)

27
Fig. 4.12: The density averaged axial velocity profile at a background pressure of 20 Pa. The line represents the local speed of sound calculated from the parallel temperature.

Fig. 4.13: The density averaged axial velocity profile at a background pressure of 100 Pa. The line represents the local speed of sound calculated from the parallel temperature.
Fig. 4.14: The axial profile of the averaged parallel temperature and of the perpendicular temperature at a background pressure of 20 Pa in a pure hydrogen expansion. The difference between the two components ahead of the shock is not yet well-understood.

where $m_{eff}$ is the effective mass of the expanding gas mixture. In this expansion the maximum velocity equals 10800 m/s and this value has not yet been reached at the beginning of the shock neither at 20 Pa nor at 100 Pa. This could be due to the uncertainty in the source temperature so in the maximum velocity or due to the fact that the stagnation pressure was not high enough to increase the velocity to its maximum. The fact that the supersonic distribution does not increase any more after the beginning of the shock opposes the latter argument. At a pressure of 20 Pa the velocity at approximately 42 mm is 3000 m/s, equal to the local sound velocity. This is the location of the Mach-disk. At 100 Pa the Mach disk is located at around 35 mm. There is a big difference in the location of the Mach disk following from the velocity profile and from the temperature profile. This comes from the uncertainty in the determination from the velocity. Since most of the particles in the expansion are hydrogen molecules the expansion will be mainly determined by H$_2$. The sound speed should therefore be calculated using an effective mass of 2 amu. The hydrogen velocity could however still be a little higher due to partial decoupling. This gives a large uncertainty in $z_M$. In the subsonic domain the H atom axial velocity decreases because the atoms share momentum with the background gas.

Using the Rankine Hugoniot relations 2.8 and 2.9 the Mach number at the beginning of the stationary shock wave can be calculated from the temperature jump. At a background pressure of 20 Pa using $\gamma = 1.55$ the temperature jump over the shock equals $\frac{T_2}{T_1} = 2.7$ resulting in a Mach number of 2.7 before the shock. Another estimation of $M_1$ can be made using the ratio of the velocities at the beginning and at the end of the shock $\frac{v_1}{v_2} = 2.2$. The resulting Mach number is $M = 1.8$. From the measured axial velocity and temperature profile the Mach number at the beginning of the shock can also be determined. It is equal to the ratio of the velocity and the sound speed $M = \frac{v_1}{c_1} = 3.4$. This clearly differs from
the value calculated from the velocity and temperature jump. One can conclude that the Rankine Hugoniot relations do not apply to this shock structure. Since one of the relations, equation 2.8, is derived on the basis of forward flux conservation one can conclude that the forward flux is not conserved in this case. This is the same conclusion as can be drawn from the lack of a density jump.

The averaged temperature along the jet centerline measured in parallel direction has been compared with the one measured in perpendicular direction, see figure 4.14. In the supersonic part the parallel temperature decreases slower than the perpendicular temperature, starting lower and ending higher before the shock. The shock front of the parallel temperature is located appr. 4 mm behind the shock front of the perpendicular temperature. This difference ahead of the shock is not yet well-understood. In the shock and in the subsonic part the temperatures are approximately equal. In the shock region and in the subsonic part the temperatures are expected to be equal since H atoms undergo numerous collisions.

4.2.3 Isotopic effect

In order to study the influence of the mass on the transport of radicals and particularly on the confinement of radicals, deuterium has been added to the hydrogen plasma and the deuterium atoms have been monitored. The experimental conditions were 3.1 slm H₂ and 0.4 slm D₂, at an arc current of 55 A and a voltage of 155 V. The stagnation pressure inside the arc channel was not influenced by the replacement.

The deuterium axial density profile of the D₂/H₂ expansion at a pressure of 20 Pa is compared to the hydrogen profile in a pure H₂ expansion in figure 4.15. The location of the beginning of the shock and the Mach disk are equal to the hydrogen situation. The slope in the supersonic regime is equal meaning that in spite of the higher mass the confinement of the D atoms is equal to that of H atoms. The higher diffusion loss for H atoms is probably smaller than the
Fig. 4.16: The H atom radial density profile at 30 mm and 20 Pa. The expansion is not overexpanded for the H atoms since the density in the core is higher than the density in the jet surroundings.

Throughout the stationary shock wave the density profile is also comparable to the hydrogen profile. In the subsonic domain the H atom density decreases slightly faster than the deuterium atom density meaning less diffusion loss to the sides, so a better transport of D atoms. The influence of the mass was already studied in the Ar-H$_2$ plasma expansion [11].

The temperature profile of the deuterium atoms in the D$_2$/H$_2$ expansion is also shown in figure 4.15. The temperatures are approximately equal along the expansion axis. In the shock region the D atom temperature is a factor of 1.2 higher. This is caused by the better energy exchange in a D/H$_2$ collision, due to the equal mass, as compared to H/H$_2$ collisions.

### 4.3 Transport in radial direction

In figures 4.16 and 4.17 the H atom radial density and temperature profile at an axial position of 30 mm from the arc and 20 Pa background pressure has been plotted. In the core of the jet the density is high, $4 \cdot 10^{20}$ m$^{-3}$ compared to its surroundings with $9 \cdot 10^{19}$ m$^{-3}$. The H atom expansion is not overexpanded since the density profile is higher near the jet centerline than in the surrounding, contrary to the neutrals in a normal gas expansion. This is due to the loss of H by diffusion induced due to the wall recombination.

The temperature in core of the jet is approximately 1000 K. When moving to the outside the temperature slightly increases to 1100 K at around 10 mm of the center due to collisions with the background gas. Then it gradually decreases further to around 500 K in the surroundings of the jet due to heat transfer to the wall.
The H atom radial velocity component profile at 30 mm and 20 Pa is plotted in figure 4.17. The velocity first increases to a maximum value of around 500 m/s at a radial position of around 10 mm when going from the expansion axis to the outside. Then the velocity decreases again to values around zero in the surrounding of the jet. This picture is in agreement with the temperature profile. It expands from the core of the jet to the outside, increasing the velocity. Then the number of collisions in the background increase and the particles are slowed down and the temperature goes up, due to conversion of directed motion into random thermal energy.

Note that the radial flow at this axial position of 30 mm, i.e. near the Mach disk, is subsonic along the radius. The speed of sound at 10 mm is around 3000 m/s which is much higher than the flow velocity. This indicates that near the end of the stationary shock wave, i.e. near the Mach disk, the barrel shock has already ended, and the radial velocity is already subsonic.

4.4 D2 vessel injection

In order to check whether D2 re-enters the plasma jet, 0.4 slm deuterium has been seeded into the background gas, while generating a plasma jet from 3.5 slm H2 gas. Deuterium atoms are then produced mainly via the following reaction

\[ H + D_2 \rightarrow HD + D \quad k = 3 \cdot 10^{-19} \text{ m}^3\text{s}^{-1} \ [23] \] (4.4)

In the expansion D atoms are monitored. In figure 4.18 the D atom radial density profile has been plotted. From the graph it can be seen that the maximum density is located around 30 mm. From figure 4.16 it follows that this is the jet boundary. The fact that there are D atoms in the jet while D2 has been injected in the background shows that deuterium molecules diffuse into the jet, even at 5 mm D2 molecules are able to cross the shock wave structure.

In figure 4.19 the D atom axial density profiles along the jet centerline have been measured at two pressures. At 100 Pa the density increases from 10 mm until 200 mm where the density
is equal to \(3.4 \times 10^{17} \text{ m}^{-3}\). Then it start to decrease. At 20 Pa the density is constant until 20 mm. After that it increases until \(9 \times 10^{16} \text{ m}^{-3}\) at 500 mm.

Assuming that the main loss mechanism of D is diffusion, approximated by \(\frac{n_D}{\tau_D}\) where \(\tau_D\) is the D atom diffusion time, one could estimate the expected D density in the subsonic part by

\[
n_D = k n_H n_{D_2} \tau_D
\]  

(4.5)

The D atom diffusion time can be approximated by

\[
\tau_D = \frac{R}{v_{th}}
\]  

(4.6)

with \(R\) the dimensions of the vessel and \(v_{th}\) the thermal velocity. This leads to a residence time of 60 \(\mu\)s at 1000 K. Using an H atom density of \(4 \times 10^{15} \text{ m}^{-3}\) from figure 4.5 at 100 mm and 20 Pa, and an estimated deuterium density of \(10^{20} \text{ m}^{-3}\) from CARS on \(\text{H}_2\) [23] a D atom density at 100 Pa of \(7 \times 10^{16} \text{ m}^{-3}\) is expected. This is in perfect agreement with the measurement.

The axial profile could now be explained as follows. Ahead of the Mach disk some deuterium molecules will already enter, but they may not yet be mixed completely. Directly behind the stationary shock wave deuterium molecules fully mix with the jet particles. In the subsonic part the \(\text{D}_2\) density will therefore increase in the beginning of the subsonic region. This means that more and more D atoms will be produced since the H atom density decreases only slowly. At some point however the loss of D atoms by diffusion towards the wall where they recombine will get larger than the production, leading to a decrease of the D density. This can be observed in the 100 Pa situation. At 20 Pa the production of D atoms is less since there are less H atoms.
Chapter 5

CONCLUSIONS AND RECOMMENDATIONS

Hydrogen atoms inside an expanding thermal plasma created from $\text{H}_2$ gas have been monitored throughout the expansion. H atom velocities, velocity distribution functions, temperatures and densities have been determined. The H atom densities have been successfully calibrated using krypton.

It has been shown that the H atoms exhibit an anomalous shock wave pattern. The temperature, densities and velocities show that a stationary shock wave is present. The density however is in disagreement with the expected behavior. The H atoms appear to be able to escape the plasma jet breaking the conservation of the forward flux. The H atoms can diffuse out of the jet because of large density gradients between the core of the jet and its surroundings, induced by the recombination of H atoms on the vessel walls. From the measurements it has also been deduced that the Rankine Hugoniot relations do not hold pointing again to the non-conservation of the forward flux.

The supersonic part of the expansion at a background pressure of 20 Pa has been shown to be non-adiabatic with an isentropic coefficient of 1.55. From the radial profile at 30 mm from the source it has been deduced that the H atom expansion was not overexpanded since the stagnation pressure inside the core of the jet was always higher than the H atom stagnation pressure in the surrounding of the jet. The hydrogen plasma expansion has been seeded with a little flow of deuterium. The deuterium atoms have been monitored throughout the expansion. It appeared that the D atom expansion is similar to the H atom expansion. Both species were able to easily escape the jet in the supersonic part and in the stationary shock wave. In the background the D atom transport was slightly better than that of H atoms due to a better confinement.

Throughout the stationary shock wave the velocity distribution function was found to be not Maxwellian. This points to a non-equilibrium situation. It appeared that like Mott-Smith proposed, the velocity distribution function could be approximated very well by two Maxwellian terms. These term had separate velocities and temperatures belonging to a supersonic and a subsonic part. Moving trough the shock the particles change from the supersonic to the subsonic distribution. From the ratio of the velocities of both distributions, information about the particles the H atoms collide with can be deduced. The H atoms probably collide with $\text{H}_2$, since most of the particles in the jet are $\text{H}_2$ molecules. It is possible that H atoms collide with H$_2$ molecules re-entering the plasma jet from the side. Re-entry of hydrogen molecules is in principle possible due to the large mean free paths near the shock front.

It has been shown that deuterium molecules are able to penetrate the barrel shock and enter
the expansion. This has been done by seeding deuterium in the background of a pure hydrogen plasma expansion. The deuterium atoms react with the H atoms forming D atoms. These D atoms have been monitored inside the plasma jet. It has been shown that already in the supersonic part and in the stationary shock wave D atoms were present pointing to the entry of D2 molecules.

The reentry of molecules into the plasma jet is an important issue. It plays a role in the shock formation but it is also of importance for the mixing with the ambient gas, e.g. the mixing of the precursors with the jet. Therefore this reentry should be studied more extensively. The first experiments should be a more detailed mapping of the D atoms in the case of deuterium vessel injection. Especially ahead of the shock front and in the beginning of the stationary shock wave. A second experiment could be made by vessel injection of krypton. This has the advantage that no reaction is needed to be able to measure it like was the case for D2. A disadvantage is the mass making it more difficult for krypton to reenter the jet.

These experiments can be done easily since the experimental arrangement is ready. To unambiguously prove that H2 reenters the plasma jet and to directly show that H atoms recombine at the wall one has to build a setup to monitor the molecules directly. In the second part of the report some detection schemes and an experimental setup for measuring H2 and D2 will be presented.
Part II

MOLECULES
Chapter 6

INTRODUCTION

The initial objective of this graduation project was to design, install and test an experimental arrangement which is able to generate vacuum UV radiation in order to probe the ro-vibrational distribution of ground state molecular hydrogen. The experiments were focussed on the measurements of the non-linear optical effect used to produce the radiation and to the measurement of the emission spectrum of the plasma. This part of the report is about the work done on the vacuum UV experiment.

Plasma-wall interaction is becoming more and more a major subject in plasma physics. The surface recombination of atoms to form molecules, is believed to have a large influence on the particle transport and the plasma chemistry [8, 23]. Hydrogen atoms for example can recombine on surfaces to form hydrogen molecules with probably high rovibrational excitation [24, 25, 26]. This process is of importance for a broad field in physics. It is of interest for plasma chemistry, e.g. the fast deposition of layers and the etching of microstructure. Plasma-wall interaction is also of interest in astrophysics, e.g. the formation of molecules on dust particles, and in fusion, e.g. in the divertor region of a tokamak reactor.

In order to understand the hydrogen wall recombination one has to study both the incoming atoms (by TALIF) and the formed molecules. The molecules are believed to have a high rovibrational excitation in the electronic ground state [24, 25, 26]. To probe these molecules one needs laser radiation in the vacuum UV region since the energy gaps to the excited states are very large. Tunable radiation at these wavelengths can only be generated using non-linear optical effects.

Another reason for monitoring H₂ molecules has already been given in part I. The transport of H₂ and its possible re-entry into the plasma jet.

In this part of the report first the different possible diagnostic methods will be discussed. Then Stimulated Anti-Stokes Raman Scattering, the process used to produce the VUV radiation will be looked at. The experimental setup will be explained in detail and the tests of the SARS process will be presented. The measured emission spectrum of an expanding H₂ plasma is also presented. It is of importance since background radiation may increase the detection limit of the optical diagnostic system. Finally, the conclusions and outlook will be given.
OPTICAL DETECTION OF H$_2$ IN A PLASMA

To get a good understanding of the wall recombination process the molecular hydrogen rovibrational population distribution in the electronic ground state of hydrogen has to be measured. The diagnostic technique should be both spatially resolved and non-intrusive. The expected density for the higher vibrational levels of the hydrogen molecules in front of a surface is in the order of 10$^{15}$ m$^{-3}$ and the detection limit should be lower than this value. The lower vibrational numbers have a slightly higher population (10$^{17}$ m$^{-3}$) and can be measured by Coherent Anti-Stokes Raman Scattering (CARS) [23]. The only methods to meet the requirements of spatial resolution and non-intrusive origin are optical methods of which only Resonance Enhanced Multiple Photon Ionisation (REMPI) and Laser Induced Fluorescence (LIF) can reach the low detection limit. REMPI, however, is difficult to apply because the plasma makes it difficult to collect the electrons/ions. So the method most suited to the requirements is LIF.

For a LIF experiment first a suitable transition should be found. In order to do this one has to know the selection rules. For molecules these rules have been derived in appendix B. In the next section a theoretical expression for the LIF signal will be derived. Then the different possible schemes to detect ground state hydrogen molecules will be discussed and the detection limits will be given.

7.1 Theoretical LIF signal

To estimate the detection limit, the LIF signal at a given laserpower should be calculated. Suppose a three level system (1,2,3) where the excited state 3 is populated by a laser. The population $n_3$ is given by [27]

$$\frac{dn_3(t)}{dt} = R(t)n_1(t) - (A + Q + \Gamma)n_3(t)$$

(7.1)

where $R(t)$ is the excitation rate, $n_1$ is the ground state population, $A = \sum_i A_i$ is the total fluorescence rate of the upper level, $Q$ the quench rate and $\Gamma$ the ionisation rate. In case of no ionisation we obtain

$$n_3(t) = n_1 \int_0^t R(t')e^{-(A+Q)(t-t')}dt'$$

(7.2)
The fluorescence is usually observed in only one channel, e.g. the fluorescence to level 2, $A_{32}$. The number of detected photons is then given by,

$$n_{LIF} = A_{32}F \int_0^\infty n_3(t)dt = ... = n_1 \frac{A_{32}}{A+Q} \int_0^\infty R(t)dt$$

(7.3)

where $F$ takes the detection efficiency into account. $F$ is given by $F = V_{det} \Omega T$ with $V_{det}$ the detection volume, $\Omega$ the solid angle and $T$ the transmission of the detection optics. When describing a one photon transition in terms of the Einstein absorption coefficient $B_{13}$ and when stimulated emission is neglected, the excitation rate is given by

$$R(t) = B_{13} = \frac{B_{13}}{c} \int I(t)g(\Delta \nu)$$

(7.4)

with $c$ the speed of light and $I(t)$ the laser pulse energy per unit area in Jm$^{-2}$. When taking the interaction between the laser profile and the line profile into account $I(t)$ has to be splitted into $\tilde{I}(t)$ the laser power amplitude at time $t$ in the pulse per unit area (in Wm$^{-2}$) and $g(\Delta \nu)$ the normalised line profile of the transition (in s). For hydrogen atoms the Doppler width is considerably larger than the laser line width, therefore $g$ can be approximated by the inverse of the Doppler width. The total amount of detected photons will then be given by

$$n_{LIF} = n_1 \frac{A_{32}}{A+Q} \frac{B_{13}}{c} \int I(t)g(\Delta \nu)$$

(7.5)

with $\tilde{I}$ the integrated laser pulse energy per unit area (in Jm$^{-2}$).

For a two-photon transition the excitation rate is expressed in terms of the cross section,

$$R(t) = G^{(2)} \sigma^{(2)} g(\Delta \nu) \left( \frac{\tilde{I}(t)}{h\nu} \right)^2$$

(7.6)

where $G^{(2)}$ is the photon stochastic factor [28] which equals 2 for a stochastic multimode field, which is the case for a dye laser. $\sigma^{(2)}$ is the generalised two-photon excitation cross section. The total number of detected photons will then be

$$n_{LIF} = n_1 \frac{A_{32}}{A+Q} G^{(2)}(\Delta \nu) \frac{\sigma^{(2)}}{(h\nu)^2} \frac{\tilde{I}^2}{t_p}$$

(7.7)

where the pulse length $t_p$ of the laser arises from the integration of $\tilde{I}^2$ over time. For the integration the pulse is assumed to be a square pulse in time.

### 7.2 H$_2$ detection schemes

The main problem measuring the ground state of light molecules is the large energy gap to the first excited state. This can for example be seen in figure 7.1 where a part of the potential
energy diagram of molecular hydrogen is plotted. A more complete potential energy diagram is given by Sharp [29] and is plotted in appendix A. The energy gap between the ground state and the first excited state is in the range 7.5 - 13 eV. For electronically exciting a molecule photons with a wavelength shorter than 175 nm are thus needed. These photons are difficult to generate and are absorbed in air.

Three different detection schemes for the detection of ground state H\(_2\) are investigated. The first uses a single photon transition with vacuum UV photons. The second scheme, referred to as UV-TALIF, uses a two-photon transition with radiation above 200 nm. The third scheme, referred to as SARS-TALIF, also uses a two-photon transition but with radiation below 200 nm.

**VUV-LIF** The first scheme is shown in figure 7.1(a). Ground state H\(_2\) molecules are excited to the \(B\) state. This transition is single photon allowed (\(\Delta \Lambda = 0, + \rightarrow +, g \rightarrow u\)) with high transition probabilities (several times \(10^8\) s\(^{-1}\)) [30]. A detailed table of all the possible transitions and transition probabilities of this so called Lyman band is given by Abgrall [30]. The lowest vibrational level that can be measured using transmitting optics is the \(v = 4\) state since below 115 nm (needed for \(v = 4\)) the optics absorb most of...
The number of fluorescence photons has been calculated using formula 7.5 and using the parameters listed in table 7.1. Using a H$_2$ density of $10^{16}$ m$^{-3}$, $2.4 \times 10^4$ photons will reach the detector. From this number a detection limit can be calculated when the background, e.i. the plasma light emission, is known. Therefore the plasma emission spectrum has been measured, see chapter 11. When there are no emission photons every photon could in principle be detected. There are however a number of limiting factors, like the detector efficiency and fluorescence wavelength, and like the plasma emission. Therefore it is more realistic to choose a lower limit of 100 photons, leading to a detection limit of $10^{14}$ m$^{-3}$ for the higher vibrational levels.

<table>
<thead>
<tr>
<th>$n_0$ in m$^{-3}$</th>
<th>VUV-LIF</th>
<th>UV-TALIF</th>
<th>SARS-TALIF</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{32}/A_{1+Q}$</td>
<td>$10^{16}$ (v=7)</td>
<td>$10^{19}$</td>
<td>$10^{19}$</td>
</tr>
<tr>
<td>$B_{13} = \frac{g_3 \lambda_3^3 A_{81}}{g_1 \delta_{sh}}$ in m$^3$J$^{-1}$s$^{-1}$</td>
<td>0.36</td>
<td>0.4</td>
<td>0.49</td>
</tr>
<tr>
<td>$G^{(2)}$</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>$\sigma^{(2)}$ in m$^4$</td>
<td>$2.0 \cdot 10^{-44}$</td>
<td>$2.0 \cdot 10^{-44}$</td>
<td>$2.0 \cdot 10^{-44}$</td>
</tr>
<tr>
<td>$g(\Delta \nu) = \frac{1}{\Delta \nu_{\text{Doppler}}}$ in s</td>
<td>$3.1 \cdot 10^{-11}$</td>
<td>$3.1 \cdot 10^{-11}$</td>
<td>$3.1 \cdot 10^{-11}$</td>
</tr>
<tr>
<td>$\bar{I}$ in Jm$^{-2}$ ($w_{\text{focus}} = 10$ $\mu$m)</td>
<td>$3.2 \cdot 10^2$</td>
<td>$1.6 \cdot 10^6$</td>
<td>$3.2 \cdot 10^5$</td>
</tr>
<tr>
<td>$h\nu$ in J</td>
<td>$9.9 \cdot 10^{-19}$</td>
<td>$1.0 \cdot 10^{-18}$</td>
<td>$1.0 \cdot 10^{-18}$</td>
</tr>
<tr>
<td>$t_p$ in s</td>
<td>$8 \cdot 10^{-9}$</td>
<td>$5 \cdot 10^{-9}$</td>
<td>$5 \cdot 10^{-9}$</td>
</tr>
<tr>
<td>$V_{\text{det}}$ in m$^3$</td>
<td>$3.1 \cdot 10^{-13}$</td>
<td>$3.1 \cdot 10^{-13}$</td>
<td>$3.1 \cdot 10^{-13}$</td>
</tr>
<tr>
<td>$\Omega_{4\pi}$</td>
<td>$1.3 \cdot 10^{-3}$</td>
<td>$1.3 \cdot 10^{-3}$</td>
<td>$1.3 \cdot 10^{-3}$</td>
</tr>
<tr>
<td>$T$</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>$n_{\text{LIF}}$</td>
<td>$2.4 \cdot 10^4$</td>
<td>$5.2 \cdot 10^4$</td>
<td>$2.9 \cdot 10^4$</td>
</tr>
</tbody>
</table>

Tab. 7.1: Parameters used for the calculation of the number of fluorescence photons impinging onto the detector for the three different detection schemes. For the VUV-LIF scheme the transition $X(v'' = 7) \rightarrow B(v' = 1) \rightarrow X(v'' = 7)$ at 152 nm is used. A temperature of 1000 K has been to determine the Doppler width. For the UV-TALIF $v''(X) = 0, v'(EF) = 0, v''(B) = 0$ and for the SARS-TALIF $v''(X) = 0, v'(EF) = 6, v''(B) = 1$
To overcome some of the problems of the first scheme two other detection schemes, shown in figure 7.1(b), are proposed. Instead of using VUV photons, which are difficult to produce and transport, two photons in the UV range are used as in the TALIF experiments. The $EF$ state is excited from the ground state by two photons. Both the $X$ and the $EF$ states are $\Sigma^+$ so the transition is two-photon allowed. Via the fluorescence to the $B$-state in the red and IR range the ro-vibrational levels of the ground state can be probed. Using this scheme in principle all the vibrational levels of the ground state of $H_2$ can be probed. One can now apply the scheme in two ways, depending on the generation of the UV photons.

**UV-TALIF** Above 200 nm the TALIF setup described in section 3 can be used. Since crystals with non-linear optical properties are used one can not go below 196 nm because the phase matching condition can not be fulfilled any more. Below 200 nm the efficiency is already so low that one can not produce enough laser intensity. This scheme uses the UV photons to excite $H_2$ to the lower vibrational levels of the $EF$ state. This state will then radiate again to the $B$ state. The number of fluorescence photons arriving at the detector has been calculated using the parameters from table 7.1. Since the two-photon cross section for this transition has never been measured and no calculated value could be found it has been approximated by the measured cross section for the transition to the $EF(v = 6)$ state. The number of photons reaching the detector at a density of $10^{19}$ m$^{-3}$ is $5.2 \cdot 10^4$. This gives a detection limit of around $10^{17}$ m$^{-3}$ using the lower limit of 100 photons. The real detection limit for the vibrational ground state however is much higher since the fluorescence signal is at 1.11 $\mu$m and detectors are very inefficient at these wavelengths. With a density of $10^{20}$ m$^{-3}$ and a quantum efficiency of the photomultiplier tube of $3 \cdot 10^{-4}$ only 150 photons would be detected. The detection limit can then be estimated to be between $10^{19}$ and $10^{20}$ m$^{-3}$. The detection limit for the vibrationally excited states is $10^{17}$ m$^{-3}$ since the fluorescence is at a lower wavelength which can be detected more efficient.

This introduces the upper limitation in the number of the vibrational levels that can be detected using the presented UV-TALIF system. At the levels $v > 4, 5$ the density will be lower then the detection limit of $10^{17}$ m$^{-3}$ and $H_2$ can not be detected. So this method is suited to measure $H_2$ in the vibrational states $v = 1 - 4, 5$ and additionally, when using high densities, the $v = 0$ state.

**SARS-TALIF** The third scheme excites ground state $H_2$ to the $v = 6$ level of the $EF$ state. To probe the vibrational ground state for example photons at 193 nm are used. This scheme has been previously applied using both ArF excimer laser and Raman shifted Nd:Yag pumped dye lasers [31]. In the SARS case the number of fluorescence photons has been calculated to be $2.9 \cdot 10^4$ at a ground state $v = 0$ density of $10^{19}$ m$^{-3}$. The detection limit is then in the order of $10^{17}$ m$^{-3}$ using the realistic 100 fluorescence photons reaching the detector. This has been calculated using the known two-photon cross section. Due to the low density in the higher vibrational states this technique is suited for the vibrational states $v = 0 - 4, 5$. A large advantage is that the setup can be identical to the VUV-LIF setup, which will be presented later, but it does not have to be used under vacuum. It can therefore be used for the alignment of the VUV-LIF setup.

Another issue is the calibration of the densities, since the densities measured by LIF are
relative. For the SARS-TALIF experiment the density can be calibrated using H\textsubscript{2} gas (mainly H\textsubscript{2}(v = 0)). The higher vibrational states however can not be produced directly, since one can not easily produce a well known amount of vibrationally excited H\textsubscript{2} molecules. Assuming that the cross sections are known or can be calculated or estimated for all the vibrational states, the levels with (v ≥ 1) can be calibrated using the calibration for v = 0. The calibration of the SARS-TALIF experiment can then be used to calibrated the VUV-LIF experiment since the setup is identical. For the UV-TALIF method the calibration has to be done using H\textsubscript{2} gas at a higher pressure. Once the system is calibrated for the vibrational ground state of H\textsubscript{2}, all other vibrational states can be calibrated if the cross sections are known.
Chapter 8

STIMULATED ANTI-STOKES RAMAN SCATTERING

In order to probe the $H_2$ groundstate using the VUV-LIF and SARS-TALIF schemes one needs photons below 200 nm, i.e. in the VUV range. These photons can be produced via several different non-linear optical techniques [32]. Since most of the vibrational levels have to be probed a widely tunable source (120 nm to 170 nm) is needed, thus Excimer and Raman lasers are not suited. Because the different resonances have to be spectrally resolved one also needs a narrowband source that can be easily tuned over the resonance. Of the two remaining techniques, Third Harmonie Generation (THG) in gases and Stimulated Anti-Stokes Raman Scattering (SARS), SARS is the best possibility since tuning is difficult with THG. THG is mainly used in the Extreme UV (XUV) region, since SARS only gives very low power because of the high order used [33].

SARS is a coherent Raman process where the incoming laser beam generates different blue and red-shifted beams in a gas. The energy diagram is shown in figure 8.1. In principle SARS is a four wave mixing process where all waves, incoming and outgoing, interact together at the same time. For simplicity however the process will be looked at as if it was a stepwise process. First a laser photon excites a molecule of the Raman medium to a virtual level. This level will deexcite again to a lower level. Radiation back to the groundstate can not be distinguished from the pump photons so it will not be taken into account. The most probable radiation is then to the first vibrational excited level, $v = 1$. The energy of this red-shifted Stokes photon is smaller than the pump photon by the vibrational shift, the so called Raman shift. The wavelength will be accordingly larger. This process is a usual Raman process. In homonuclear diatomic molecules the resulting level, $v = 1$ can only be depopulated by collisions. It can however be excited by another laser photon to a higher virtual level. This level can radiate to the groundstate and the resulting first Anti-Stokes (AS) photon will have an energy larger by the Raman shift. The wavelength will then be blue shifted. The proces is the same as the CARS process and can be seen at the left hand side in figure 8.1.

The $v = 1$ level can also be excited by the Anti-Stokes photon and the resulting second order Anti-Stokes photon will be even more blue shifted. This process can repeat several times the $(n + 1)$-th order Anti-Stokes being produced by both a laser photon and a $n$-th Anti-Stokes, see the right hand side of figure 8.1. Since the first Stokes is used in the production of all the anti-Stokes its energy and stability are very important. A possibility to improve the stability of the Stokes and the higher anti-Stokes is Stokes seeding [34]. In this case a small amount of light at the first Stokes wavelength is seeded into the Raman cell to stabilise the generation
of the first Stokes wavelength. The frequency and wavelength of the \( n \)-th Anti-Stokes is given by the following formula.

\[
\omega_{ASn} = \omega_{pump} + n\Omega \quad \text{or} \quad \lambda_{ASn} = \frac{\lambda_{pump}}{1 + n\lambda_{pump}\Omega}
\]  

(8.1)

with \( \omega \) the wavenumber, \( n \) the order, \( \Omega \) the Raman shift and \( \lambda \) the wavelength.

In figure 8.1 also the momentum conservation of the process is shown. Due to the momentum conservation the Anti-Stokes beams are slightly non-colinear. The angle with the laser beam is in the range 0.5 - 1\(^{\circ}\).

SARS is a non-linear optical effect that originates from the polarisation \( P \),

\[
P = \chi^{(1)} \cdot \vec{E} + \chi^{(2)} : \vec{E}^2 + \chi^{(3)} : \vec{E}^3 + \ldots
\]  

(8.2)

with \( \chi^{(n)} \) the \( n \)-th order susceptibility and \( \vec{E} \) the electric field.

Since usually only relatively low electric field are used, the higher orders can be neglected and the polarisation is considered to be proportional to the electric field, \( \chi^{(n)} = 0 \) for \( n > 1 \), the classical electromagnetism situation. Non-linear optical effects however originate from the higher order terms and the linear approximation is no longer valid. Due to symmetry considerations the odd terms vanish when using solid media and the even terms vanish when using gaseous media. The SARS process originates from the third order susceptibility \( \chi^{(3)} \).

The difficulty in solving is first that \( \chi^{(3)} \) can only be calculated using quantum mechanics, and second that all the waves are coupled together. This considerably complicates solving the Maxwell equations. The details are given by [35].

The production of the first Stokes is a very important step in the process since the production of all the anti-Stokes depends on it. Therefore the so-called Raman gain coefficient \( g_s \), the gain
of the first Stokes is an important factor [34].

\[ g_s = \frac{16\pi^2 e^2}{\hbar n_s^2 \omega_0 \omega_s} \frac{\Delta n}{\Delta \omega_R} \frac{d\sigma}{d\Omega} \] (8.3)

where \( n_s \) is the refractive index at the Stokes frequency, \( \omega_0, \omega_s \) are the frequencies of the pump photon and the Stokes photon respectively, \( \Delta n \) is the population difference between the states involved, \( \Delta \omega_R \) is the Raman linewidth and \( \frac{d\sigma}{d\Omega} \) is the differential Raman cross section.

To have a relatively high energy output at the shifted wavelengths the Raman medium should have a large Raman cross section. Since the AS intensity drops quickly with the order it is favourable to use a low order AS for probing. This can be achieved by Raman media with a large Raman shift. Another requirement is that the Raman medium is transparent to the generated radiation. Hydrogen fits these requirements very well and is therefore often used as Raman medium. The Raman shift for hydrogen is the largest of all molecules (4155.25 cm\(^{-1}\)) since its mass is the lowest.

In order to improve the Raman process the hydrogen is often cooled down to liquid nitrogen temperature. The effect on the rotational population can be calculated as follows. At 293 K the rotational distribution is fully thermalised and can be calculated by

\[ n = \frac{N_{tot} \ g_I \ (2J + 1) \ \exp \left( \frac{-BJ(J+1)}{kT} \right)}{F_{tot}} \] (8.4)

where \( n \) is the relative population, \( N_{tot} \) is the total number of molecules in the \( v = 0 \) state and \( J \) is the vibrational quantum number. \( B \) is the rotational constant (60.8 cm\(^{-1}\) for H\(_2\)), \( k \) the Boltzmann constant and \( T \) the temperature. \( F_{tot} \) is the total partition function which is used as a normalisation factor. \( g_I \) is a factor originating from nuclear spin statistics. For hydrogen there are two types of nuclear spin waveforms, a symmetric and an anti-symmetric one. Due to symmetry considerations the two kinds are linked to \( J \) [36], giving rise to two kinds of hydrogen molecules. Para-hydrogen for even \( J \) and ortho-hydrogen for odd \( J \). The transition from one kind to the other is strictly forbidden and takes very long (months). When changing the temperature the two types can not thermalise so there are two distributions. From the distribution at room temperature the amount of para- and ortho-hydrogen can be calculated,

\[ N_{tot} = N_{ortho} + N_{para} \] (8.5)

These values are used to calculate the distributions at other temperatures (e.g. 77 K),

\[ n = \frac{N_{ortho(para)}}{F_{ortho(para)}} \ g_I \ (2J + 1) \ \exp \left( \frac{-BJ(J+1)}{kT} \right) \] (8.6)

The resulting populations are shown in table 8. Since the odd levels have the higher statistical weight the level \( J = 1 \) is the main contributor at 77 K. The relative population in \( J = 1 \) increases from 0.69 to 0.75, when cooling down to 77 K. This effect is not enough to fully explain the large difference when cooling down.
The second and most important effect is the narrower Raman linewidth at 77 K, since the Stokes gain coefficient is inverse proportional to the Raman linewidth. This linewidth has a complicated pressure dependence in hydrogen since one can have pressure broadening and Dicke narrowing,

\[ \Delta \omega_R = \frac{a(T)}{n_{\text{gas}}} + b(T) \cdot n_{\text{gas}} \]  

(8.7)

where \( a(T) \) is proportional to the self diffusion constant \( \sim T^{1/2} \), and \( b(T) \) is proportional to the particle velocity \( \sim T^{1/2} \). When changing the density to the pressure \( a \sim T^{3/2} \) and \( b \sim T^{-1/2} \). So the Raman linewidth decreases when cooling down.

A third contributor is the freezing out of impurities like water vapour. All three effects together give an increase in the Stokes gain coefficient of one order of magnitude when going down from 300 K to 77 K at a pressure of 1 bar. A more detailed description can be found in literature [37, 38, 39].
Chapter 9

EXPERIMENTAL SETUP

In this chapter the VUV-LIF experimental arrangement will be described. An overview of the setup is given in figure 9.1. The different parts of the setup, the laser, the AS generation, the AS selection, the reference branch and the detection branch will be described in detail in the following sections. In the last section a quick overview of the setup for TALIF on H₂ will be given.

Fig. 9.1: An overview of the VUV-LIF setup. Behind the Raman cell all the optical paths have to be under vacuum.
9.1 Laser system

A scheme of the laser system to generate the VUV photons is shown in figure 9.2. The third harmonic (350 mJ at 355 nm) of an injection seeded Nd:YAG laser (Quanta-ray CGR-230) is used to pump a tunable dye laser. The dye laser is operated around 440 nm (Coumarin 120) with an estimated output pulse energy of 40 mJ. This beam is then frequency doubled using a BBO crystal. The resulting UV beam at 220 nm has a pulse energy of 6 mJ and is 6 ns long. It is vertically polarised and has a Lorentzian frequency profile with a bandwidth of 0.15 cm\(^{-1}\).

The system was first operated using a Spectra Physics PDL3 dye laser. The dye laser reflective optics were however not resistant to the high power of the third harmonic beam of the Quanta Ray Nd:YAG laser. Therefore a new dye laser has been ordered for the future experiments.

9.2 Raman cell

A conventional Raman cell is a long tube filled with high pressure gas, and the laser light is focussed by a long focal distance lens. The Raman cell used in our experiments has a different design, which has been introduced by H.F.Döbele et.al. [40]. This cell has several advantages. First only a small volume of the Raman medium is cooled thus avoiding numerous technical problems. Second the cell can be operated at a considerable lower pressure than in usual Raman cells. The cell is also as efficient as a usual Raman cell. A schematic is shown in figure 9.3.

Since the efficiency at which the AS photons are produced depends critically on the quality of the pump laser beam, the Raman cell is positioned in the far field of the laser beam. Here the spatial intensity distribution of the laser beam approaches a Gaussian profile. The better quality of the laser beam increases the AS production considerably. The laser beam is focussed into the Raman cell by a suprasil 120 mm focal distance plano convex lens. The focus is located inside the 3 mm diameter channel in the copper cold finger. The fanned copper
Fig. 9.3: A schematic drawing of the Raman cell. The laser beam is focussed into a cold finger at 77 K. The entrance and exit windows are insulated from the cell to prevent ice formation.

cold finger is cooled with liquid nitrogen to 77 K. To prevent water from freezing at the glass surfaces the lens and the tilted MgF\(_2\) exit window are isolated from the cell by thick plastic rings. Because the optimum pressure for generating AS beams is above 1 atm the glass dewar which has been used previously is replaced by a metal dewar to allow for operating at high pressures. It is possible to create a flow of the Raman medium (H\(_2\) gas in these experiments) through the cell.

9.3 AS selection and reference branch

A collection of Stokes and anti-Stokes beams emerge from the Raman cell. In order to select the desired AS beam and to refocus it a specific system is needed. These system are the AS selection branch and the reference branch as depicted in figure 9.1.

After the Raman cell the beams diverge into a vacuum system. To prevent backreflections into the cold finger of the Raman cell the beams exit through a tilted exit window. The AS beams are then seperated in the AS selection branch setup and the selected AS beam is focussed into the vacuum vessel. This optical system of mirror and grating is placed under vacuum to avoid absorption by oxygen. The system is seperated from the vacuum vessel by a 3 mm thick MgF\(_2\) window. The AS beams are reflected by an Al-MgF\(_2\) coated 2.25 m radius of curvature concave mirror located at a variable distance of around 1.5 m with respect to the middle of the vessel. The mirror can be adjusted from outside the vacuum chamber. The converging beams are seperated by a Al-MgF\(_2\) coated grating. The holographic 1200 lines/mm grating has a blazing angle optimised for 150 nm and can be rotated from outside the vacuum system. The first order diffraction of the needed AS beam is directed upwards and focussed by the mirror in the vacuum vessel. The measure and configuration of the AS selection optics is described.
Fig. 9.4: The reference and detection branches of the VUV-LIF experiment. The reference branch is used to measure which AS is focussed into the vacuum vessel. It is also used to correct for shot-to-shot variations in the laser intensity. The detection branch collects the fluorescence signal.

To be able to know which AS is selected and focussed into the vacuum vessel and to optimize the alignment of the beam the diverging laser beam is redirected onto the entrance slit of a 40 cm VUV-monochromator (MacPherson). The 1800 lines/mm grating is optimised for 150 nm. The entrance and exit slit width can be varied. The exiting beam intensity is attenuated by a series of metal meshes and measured by a diamond cathode solar blind PMT (Hamamatsu R7639). The time-integrated signal of the PMT is used to correct for the shot-to-shot variation in laser intensity. A scheme of the so-called reference branch is shown in figure 9.4.
9.4 Detection branch

The LIF signal can be collected in several ways. One is using a 10 cm diameter 275 mm focal distance MgF$_2$ lens. The solid angle covered by the clear aperture of the lens (80% of the lens area) is then $7 \times 10^{-2}$. The detection setup is shown in figure 9.4. A diaphragm is used to reduce the stray light. The signal is then focussed onto a slit to define the detection volume and the intensity is measured by a solar blind PMT (Hamamatsu R7639). A variant which can be used when the amount of background radiation is too high is focussing the signal onto the entrance slit of a 20 cm VUV monochromator (Minuteman). The 1 mm width exit slit gives rise to a spectral resolution of 7 nm. The monochromator is thus used as a spectral bandpass filter to filter out the plasma radiation such as Lyman-$\alpha$. The slit width can be reduced to increase the resolution. This will however decrease the signal intensity. The detection branch with monochromator can also be used as an emission setup to measure the plasma emission to study the recombination and (de)excitation processes. The signal is again measured using the same solar blind PMT.

A second method is shown in the overview of the VUV-LIF setup, figure 9.1. The fluorescence is focussed by a concave Al-MgF$_2$ coated mirror onto the slit of the VUV monochromator via a flat Al-MgF$_2$ coated mirror. To align all the optics in this setup is more complicated than when only using one lens. The optical aberrations however are much less and the detection volume is better defined.

A third detection method uses two Al-MgF$_2$ coated mirrors. A 15 cm diameter concave mirror is used to project the fluorescence onto a 2.5 cm diameter convex mirror which focusses the light onto the slit of the VUV monochromator via a hole in the center of the first mirror. Again the optical alignment is difficult especially under vacuum. The optical aberrations however are close to zero.

9.5 TALIF setup for detection of H$_2$

The TALIF setup used to probe H atoms, described in section 3, can be used to detect H$_2$ following the detection scheme \( X \rightarrow EF \rightarrow B \). A scheme of the setup is drawn in figure 3.1. There are however a few differences. First the dye laser is operated around 606 nm (sulforhodamine 640). A different detector has to be used that is sensitive in the IR. A PMT (e.g. Hamamatsu R5108, R1767, R316-02 or R632-01) can be used. To decrease the anode dark current the PMT should be cooled to e.g. -30$^\circ$. This gives already a decrease in the anode dark current of a factor of $10^3$. A diode has a much better quantum efficiency $\epsilon$, the probability that a photon creates an electron at the photocathode (typically $\epsilon = 0.6$ for IR diodes and $\epsilon = 0.0003$ for IR PMT's at 1.1 $\mu$m) The gain for normal diodes however is much lower (1 compared to $10^6$ for PMT's). The gain of an avalanche photodiodes can be higher, but they are very slow compared to fast diodes and PMT's.
Chapter 10

RAMAN CELL RESULTS

In this chapter the experimental setup that is used for test experiments of the Raman cell is presented. Results on anti-Stokes production as function of pump laser power and gas pressure in the Raman cell are given. Finally the degeneration of the Raman medium will be discussed.

10.1 Anti-Stokes production

The tests of the Raman cell have been performed on the cell with the glass dewar. The experimental arrangement for these experiments is different from the setup as presented in chapter 9. The setup is shown in figure 10.1. The second harmonic (500 mJ at 532 nm) of an injection seeded Nd:YAG laser (Quanta-Ray GCR-230) is used to pump a tunable dye laser. The frequency is usually 20 Hz but can be changed to 10 Hz or even lower by changing the Q-switch timing. The dye laser is operated around 610 nm (Rhodamine 610) with an output pulse energy of 120 mJ. This beam is then frequency doubled using a KDP crystal. The resulting UV beam at 305 nm has a pulse energy of 15 mJ and is 8 ns long. It is linearly polarised and has a Lorentzian frequency profile with a bandwidth of 0.15 cm\(^{-1}\). The UV beam is focussed into the Raman cell using a 25 cm focal distance suprasil lens. The divergence of the Stokes and anti-Stokes beams is then reduced by a 30 cm CaF\(_2\) lens. The beams are separated using a suprasil Pellin Brocca prism and their intensities are measured by a pyroelectric detector.

Fig. 10.1: The setup used for testing the Raman cell
Fig. 10.2: The intensity of the different anti-Stokes (AS) and Stokes (S) beams as function of the wavelength at a repetition rate of 20 Hz. The pump energy was 11 mJ at 305 nm and the H$_2$ pressure was 1.7 bar. AS order 1 to 5 have been measured with a pyroelectric detector. AS order 5 and 6 have been measured with a VUV monochromator and a PMT.

(Ophir). A few higher order anti-Stokes have been separated and measured using a VUV monochromator (MacPherson) and a solar blind PMT (Hamamatsu R7639).

The intensities of the different anti-Stokes (AS) and Stokes (S) beams have been measured at 20 Hz. The results for 20 Hz are shown in figure 10.2. The intensity of the first to the fifth anti-Stokes beam (AS1 to AS5) and of the three S beams were high enough to be measured using the pyroelectric detector. The AS6 beam had to be measured under vacuum ($\lambda < 186 \text{ nm}$) using the VUV monochromator. The calibration in intensity was performed with AS5. The intensities shown are the intensities at the cold finger. In order to do this the measured intensities have been corrected for the transmission of the optics. Up to 6 AS and 3 S beams have been measured. The intensities of the AS5 and AS6 beams is already underestimated due to the increased absorption in the exit window of the Raman cell. Higher AS could not be measured due to the transmission limit of the fused silica exit windows of the Raman cell. S4 has been observed but its intensity was too low to be measured by the pyroelectric detector.

The intensities of the AS beams have also been measured at a repetition rate if 10 Hz. They were found to have less intensity compared to the measurements at 20 Hz. It is believed that this is due to the beam profile of the Nd:YAG laser, which is partially imaged onto the dye laser profile. This profile is worse at 10 Hz than at 20 Hz, since the Nd:YAG laser has been optimised for a repetition rate of 20 Hz.
The intensities of the 3\textsuperscript{rd} and 4\textsuperscript{th} AS have been measured as a function of the pumping power. The production of the AS is a multiple photon process. This implies that the intensities should increase with a power of two or higher of the pumping power. The intensity of the AS however is approximately linear with the input intensity both for AS3 and AS4. This has already been observed previously [40]. The produced lower AS levels are depleted by the production of the higher AS. The higher the pumping power, the higher the depletion resulting in a quasi-linear behavior of the low order AS. The higher AS levels will exhibit a non-linear behavior [40].

10.2 Optimisation of the Raman cell

The main objective of the test of the Raman cell was to check whether the SARS process was effective enough to generate sufficient AS intensity. In the previous section this was shown. The next step was to optimise the output. The first parameter to optimise was the H\textsubscript{2} pressure in the cell. The intensity of the first AS was measured as a function of the pressure at two frequencies, see figure 10.4. The output increased with the pressure. No measurements have been performed above 1800 mbar to prevent the glass dewar from breaking. Probably the optimum will be around 1900 mbar for both frequencies. This still has to be verified using the metal dewar cell.

The next parameter was the degeneration of H\textsubscript{2}. This was first tested by monitoring the first AS power during 30 minutes, the time approximately needed to make one scan of a
transition. The output power did not change during this period. On the time scale of minutes the hydrogen did not degenerate. The degeneracy on second time scale could however not be checked in this way. Therefore a flow of hydrogen has been applied through the Raman cell. With the flow of several liters per minute the volume of the cold finger was replaced by new hydrogen within one second. The output energy of the second AS as a function of the hydrogen flow is shown in figure 10.5. No influence of the hydrogen flow has been observed within the accuracy. It can be concluded that at the time scales used for the experiment the hydrogen did not degenerate and there is no need to use a flow.

Fig. 10.4: The intensity of the 1st anti-Stokes as a function of the H₂ pressure in the Raman cell for two different laser frequencies. The pump intensity was 8 mJ at the cold finger.

Fig. 10.5: The intensity of the 2nd anti-Stokes as a function of the flow of H₂ through the Raman cell at 20 Hz. The pressure has been kept constant at 1.5 bar and the pumping energy was 11 mJ.
Chapter 11

H₂ PLASMA EMISSION SPECTRUM

In order to determine the plasma emission, i.e. the background radiation, in the detection of the fluorescence photons, the emission spectrum of a pure H₂ expanding plasma has been recorded using a 20 cm Minuteman vacuum UV monochromator. The emission has been measured from 700 nm down to 110 nm. The obtained spectrum is shown in figure 11.1.

The emission spectrum in the beginning of the plasma has been measured without any imaging optics. The monochromator was simply connected to the vessel and all the light entering through the entrance slit was measured. Therefore the spectrum can not be spatially resolved. This also decreases the spectral resolution. The resolution using a 100 μm exit slit was calculated to be approximately 1 nm. The width of all the observed atomic lines however is appr. 8 nm. This is caused by the different entrance angles of the light due to the lack of imaging optics. The calibration of the monochromator was performed using an indium, a mercury, an argon and a sodium lamp complemented with the location of the Balmer α lines.

In the spectrum several atomic hydrogen lines can be seen. The Balmer series is very clearly present from H α at 656.3 nm to H 6 and ending in the n=2 continuum. Also the Lyman alpha line is present at 121.6 nm. The molecular Lyman band ranging from 135 nm to 165 nm is
the transition $H_2(B) \rightarrow H_2(X)$. Two other peaks can be seen at 305 nm and at 283 nm. The origin of these peaks is not clear yet. It is however not very important since the goal was to determine the number of emission photons at a certain wavelength.

From this measurement an estimate of the amount of background light can be made. At the peak of the Lyman band approximately $10^5$ photons are detected per second calculated from the PMT signal. Using a PMT with a 1 $\mu$s gate this means less than 1 photon during the gate. This can surely be neglected. Therefore the detection limit of the VUV-LIF experiment can be estimated in the order of $10^{14}$ m$^{-3}$.

Since there is already not much emission in the Balmer series it can be expected that there will be almost no emission at larger wavelengths. Therefore also the detection limits of the scheme using the $EF$ state are correct at $10^{17}$ m$^{-3}$.
Three different detection schemes for molecular hydrogen have been looked at. All three methods appeared to be feasible. The SARS-UV method is very well suited for detection of groundstate and low $v$ H$_2$. The TALIF-UV is well suited for the low $v$ levels but less suited for the detection of groundstate H$_2$. The detection limit for those techniques has been estimated to be in the order of $10^{17} \text{ m}^{-3}$. This is not sensitive enough for the higher vibrational states. These methods are therefore best suited for measurement of the transport properties of groundstate H$_2$. For the TALIF-UV method the existing TALIF setup can be used. For the other method the Raman cell has to be used and the setup can very well be implemented in the VUV-LIF setup.

The method using the $B$ state, e.g. the VUV-LIF experiment, is very well suited for the higher vibrational levels of the electronic groundstate. The detection limit has been estimated in the order of $10^{14} \text{ m}^{-3}$. It is thus very sensitive. The method is perfectly suited to study the wall recombination of hydrogen since it is expected that the resulting H$_2$ is highly vibrationally excited.

The combination of the SARS-UV and the VUV-LIF experiment can then measure all the vibrational levels of the electronic groundstate of H$_2$. Another advantage is the calibration of the density measurements. The VUV-LIF can be calibrated using the SARS-UV method.

An experimental setup has been designed for the VUV-LIF experiment. The Raman cell producing the vacuum UV radiation has been tested. Starting at 305 nm 6 anti-Stokes and 4 Stokes orders have been seen. The Raman cell has been optimised for pressure and the H$_2$ degeneration has been investigated and accordingly some improvements have been made in the Raman cell.

The emission spectrum of a pure hydrogen plasma has been measured in order to estimate the amount of background light. The amount of background light appeared to be negligible.

In the future first the transport properties of H$_2$ have to be investigated. Therefore a first try can be made using the existing TALIF-UV setup. Then the SARS-UV and VUV-LIF setups should be build with the new laser system to measure both the transport properties and the wall recombination of hydrogen. These measurements should be combined with the TALIF measurements on hydrogen atoms both in the plasma and in front of a surface.
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In the first place I say many words of thanks to my father who now hopefully found the rest he could not find for a very long time. I know that you would be very proud now and I know that I could not have reached this without you. And my dear mother I kiss many thanks for the support she always gave me and especially for all those years she took care of my father.

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I would also like to thank Richard Engeln. I really enjoyed working with you and I look forward to the next four years of working together. We should really start the monthly poker evening. Daan Schram I thank for all the nice discussions we have had about the results. Sometimes very confusing and difficult to follow and other times very clarifying but always helpful.

This graduation project I could not have finished without the skillful help of the technical staff, Riis, Jo, Herman and Bertus. Always present in case of problems and when help was needed. And trust me problems always come in large numbers.

Uwe Czarnetzki I thank for his immediate response and so showing us the light about SARS. And I also thank Professor Döbele for his permission to use his Raman cell design.

Last but not least I thank all the members of ETP. I enjoyed working with you all and I am certain it is going to stay like that the next four years. Maikel and Marco, I apologize for teasing you and for keeping irritating, but I must admit I liked it. And Johan, maybe in four years we will juggle with five balls simultaneously.
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Appendix A

H₂ POTENTIAL DIAGRAM

On the next two pages the potential diagram of molecular hydrogen by Sharp [29] is plotted.
Appendix B

MOLECULAR SELECTION RULES

In this chapter the emission or absorption of radiation due to transitions between the energy levels of molecules will be discussed. Because molecular spectra are far more complicated and divers than atomic spectra the discussion will be confined to diatomic molecules. First it will be explained how the molecular energy levels can be calculated. Then the symmetry of molecules will be discussed in order to derive the selection rules for transitions in the last section.

B.1 Molecular energy levels

The energy of a molecular state consists of the following parts, translation, rotation, vibration, electronic motion and electronic and nuclear spin. In first approximation these contributions are considered separable. This means the total energy is the sum of all individual contributions.

\[ E_{\text{total}} = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{elec}} + E_{\text{spin}} \] (B.1)

Quantum-mechanically this means that all Hamiltonians commute with each other. The total wavefunction can than be written as the product of all individual wavefunctions

\[ \Psi_{\text{total}} = \Psi_{\text{trans}}(x, y, z)\Psi_{\text{rot}}(\theta, \varphi, \chi)\Psi_{\text{vib}}(R)\Psi_{\text{elec}}(r)\Psi_{\text{spin}} \] (B.2)

The total energy is often plotted as a function of the internuclear distance in a so called potential energy diagram. Because the energy in the center of mass system of the molecule is considered, the translational part of the energy and wavefunction can be left out.

In the rigid rotor approximation the molecular distance is considered constant and the rotational part can be seperated from the rest. The energy is then given by [36]

\[ E_{\text{rot}} = BJ(J + 1) \] (B.3)

with \( B \) the rotational constant and \( J \) the rotational quantum number. The rotational constant is in the order of several cm\(^{-1}\). In a better approximation [36] the rotational part is not separable from some of the other terms and centrifugal distortions have to be added. The
A first classification of the molecular energy projection of the rotational angular momentum of the molecule on an external field direction $m_J$ can take on any integer value between $-J \leq m_J \leq J$. So the rotational energy exhibits a degeneracy of $g_J = 2J + 1$.

The vibrational energy can in a first approximation be calculated assuming the vibrational motion to be harmonic. The energy is then given by

$$E_{\text{vib}} = h\nu(v + \frac{1}{2})$$

(B.4)

with $v$ the vibrational quantum number and $\nu$ the vibration frequency. The vibrational energy quantum $h\nu$ is in the order of thousand cm$^{-1}$. The harmonic oscillator is only a very rough approximation as the quadratic potential curve only fits the lowest energy levels. For a better approximation one should use an anharmonic oscillator in for example a Morse potential. The vibrational part of the wavefunction is then not separable any more.

A first classification for the different electronic energy states in a potential energy diagram is the absolute value of the projection of the angular momentum of the electrons on the nuclear axis $\Lambda = |M_L|$. It defines the electronic state as shown in table B.1. Further classifications are given by symmetry considerations, which will be shown in the next section.

### B.2 Symmetry

The selection rules for transitions between different energy states in molecules depend on the initial and final wavefunction and the transition operator. The most useful way of discussing this is in terms of symmetry.

Because diatomic molecules possess a simple cylindrical symmetry, they form an relatively easy system for symmetry considerations. For more complex polyatomic molecules one has to use Group theory.

The basic procedure to find a molecules symmetry is to identify the operators that leave the molecule unchanged. There are three operators appropriate for diatomic molecules. The first is a rotation around the nuclear axis through an angle $\phi$. This is denoted by $C_\phi$. All diatomic molecules have this symmetry to some extent, depending on the angular momentum of the electrons.

The second operator, $\sigma$ is a reflection in a plane containing the nuclear axis, denoted by $\sigma$. There exist an infinite number of these mirror planes. Diatomic molecules in a $\Sigma$-state are either symmetric or anti-symmetric under this operation. The wavefunctions are denoted by $+$ or $-$ when they are left unchanged or change sign under $\sigma$ respectively. In states with

<table>
<thead>
<tr>
<th>$\Lambda$</th>
<th>Notation</th>
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<tbody>
<tr>
<td>0</td>
<td>$\Sigma$</td>
</tr>
<tr>
<td>1</td>
<td>$\Pi$</td>
</tr>
<tr>
<td>2</td>
<td>$\Delta$</td>
</tr>
</tbody>
</table>

Tab. B.1: A first classification of the molecular energy

Table: Notation

<table>
<thead>
<tr>
<th>$\Lambda$</th>
<th>Notation</th>
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</thead>
<tbody>
<tr>
<td>0</td>
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<tr>
<td>1</td>
<td>$\Pi$</td>
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<tr>
<td>2</td>
<td>$\Delta$</td>
</tr>
</tbody>
</table>
\[ \Lambda > 0 \] there do not exist an infinite number of planes any more. So the + or - states can not be distinguished. The states are therefore doubly degenerate.

For homonuclear diatomic molecules, (i.e. molecules formed by two identical atoms), there exists another symmetry, inversion through the center of mass, denoted by \( i \). This operator changes all coordinates from \( \vec{r} \) to \(-\vec{r}\) with the origin at the center of mass of the molecules. The states are labeled \( g \) (from "gerade") when they are symmetric and \( u \) (from "ungerade") when they are anti-symmetric under \( i \).

As mentioned above the notation of a molecular state depends both on \( m_J \) and on the symmetry. As an example we will treat the first excited state of the hydrogen molecule. This state is called the B-state and is an \( \Sigma^+ \). It is \( \Lambda = 0 \) state and is therefore unchanged by any rotation \( C_\phi \), denoted by \( C_\infty \), and is also nondegenerate. Under the operator \( \sigma \) it is symmetric, and under \( i \) (homonuclear) it is anti-symmetric, denoted by + and \( u \) respectively.

**B.3 Selection rules**

In order to analyze the molecular spectra one has to know which energy levels are coupled by radiation. In other words one has to know the different selection rules. To derive these rules various quantum-mechanical operators have to be examined and their symmetry properties considered. The strongest transitions are electric-dipole transitions, which are represented by the electric dipole operator \( \mu \). Some weaker transitions are the magnetic dipole and the electric quadrupole transitions, represented by the rotation operator \( J \) and the quadrupole moment tensor \( Q \), respectively. In the following only the electric dipole transitions will be considered.

**B.3.1 Electronic selection rules**

Because the transition intensity is proportional to the corresponding matrix element, the matrix elements have to be non-zero for a transition to occur. The matrix elements considered are of the form

\[
\langle \psi_1 | \mu | \psi_2 \rangle \quad (B.5)
\]

The calculation of these elements is however very complicated because of the molecular wavefunctions. Therefore the symmetry properties are used to derive the selection rules. The matrix elements can only be non-zero when they are not anti-symmetric. Since the wavefunctions of a molecule must exhibit the same symmetry as the molecule itself they must be either symmetric or anti-symmetric under the symmetry operations. Therefore the product of the initial wavefunction, the transition operator and the final wavefunction has to be totally symmetric in order for the transition to occur.

The symmetry of the dipole operator can be shown [36] to be \( \Sigma^+ \) in the direction of the nuclear axis, and \( \Pi_u \) perpendicular to the nuclear axis. The product must then be totally symmetric, i.e. have the symmetry \( \Sigma^+_u \). So in electric dipole transitions the angular moment does either not change (parallel transition) or changes by one (perpendicular transition). For
Appendix C

ANTI-STOKES SELECTION OPTICS

Fig. C.1: The scheme of the AS selection optical arrangement. The measures are in millimeters unless stated otherwise.

The optical arrangement for the AS selection is shown in figure C.1. The measures are also shown. The radius of curvature $R$ of the UV mirror was calculated to be 2.25 m. This was calculated using the formula

$$\frac{1}{b} + \frac{1}{v} = \frac{1}{2R} \Rightarrow R = \frac{2vb}{v+b} = \frac{(600+1500)(1500+910)}{(1500+910) + (600+1500)} = 2244 \text{ mm} \quad (C.1)$$

with $v$ the distance from the focus in the cold finger to the UV mirror and $b$ the distance from the UV mirror to the focus.
The focus waist was calculated using the following equation,

$$w = \frac{f \lambda}{\pi d} \approx 1 \, \mu m$$  \hspace{1cm} (C.2)

with $f = R/2$ the focal distance of the mirror, $\lambda$ the focal length (approximated by the upper limit of 170 nm) and $d$ the diameter of the beam before the system (approximated by the diameter of 20 mm on the mirror). The value of 1 $\mu m$ is a lower limit. Since the beam will not be perfectly Gaussian and because of spherical abberations a more realistic value for the focus waist is 10 $\mu m$ The focus length was approximated by two times the Rayleigh length:

$$z_{focus} = 2z_{rayleigh} = \frac{2\pi w^2}{\lambda} = 15 \, mm$$  \hspace{1cm} (C.3)