

Chapter 2

Experimental Setup

2.1 Overview of Experimental Setup

Figure 2.1 shows the overview of our experimental setup. There are three main parts: a continuous molecular beam source, an ultra high vacuum chamber and a continuous infrared excitation setup.

I discuss the details of the experimental setup used during this thesis work in the next sections. Attention is focused on the components of the experimental setup that were developed during my thesis work.

2.2 Molecular Beam Source

The continuous (CW) molecular beam source (Thermionics, MSC-9800) consists of three differentially pumped stages, shown in Fig. 2.1. The 1st stage contains a temperature-controlled (25–200 °C) homebuilt pinhole nozzle ($\varnothing = 50\text{ }\mu\text{m}$ orifice) and an electroformed nickel skimmer (Beam Dynamics, $\varnothing = 1\text{ mm}$). The nozzle is heated by an OMEGA CN8200 series temperature and process controller and a 12 V DC power supply sending current through thermal coax wrapped around the nozzle. For example, with 8 V and 0.55 A of heating power, the controller stabilizes the nozzle temperature at 150 °C. At a distance of $\sim 2\text{ cm}$ from the nozzle, the skimmer extracts the cold core of the supersonic expansion. The first stage is evacuated by a 1,000 l/s turbo pump (Balzers, TMU1000) backed by a 20 m³/h mechanical pump (Balzers, Duo 20), and has a base pressure of $<1 \times 10^{-7}$ mbar. When producing an expansion of 12% CH₄ in H₂ with a nozzle temperature of 50 °C and three bar backing pressure, the typical operating pressure is $\sim 2 \times 10^{-3}$ mbar.

The 2nd pumping stage houses a chopper wheel ($\varnothing = 127\text{ mm}$) rotating at 200 Hz driven by a water-cooled AC-synchronous motor (Globe 18A1003-2).

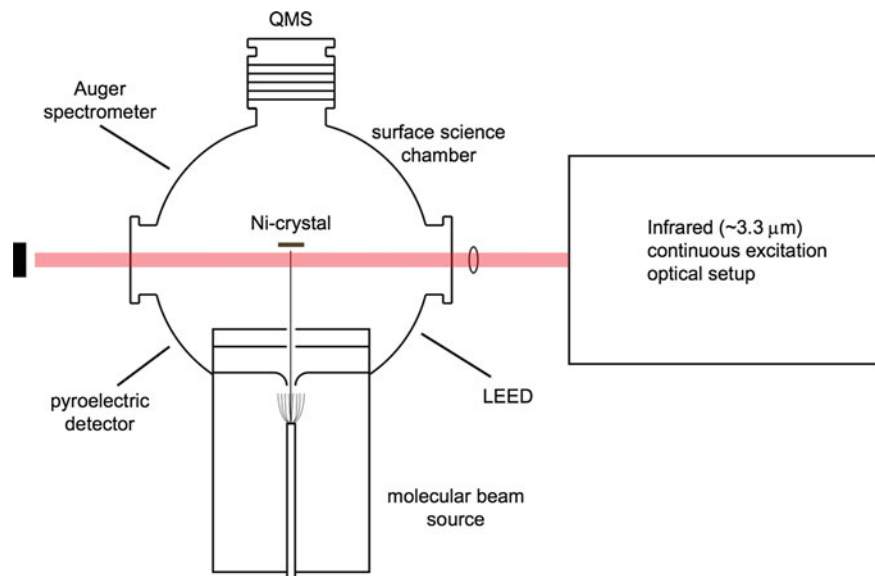
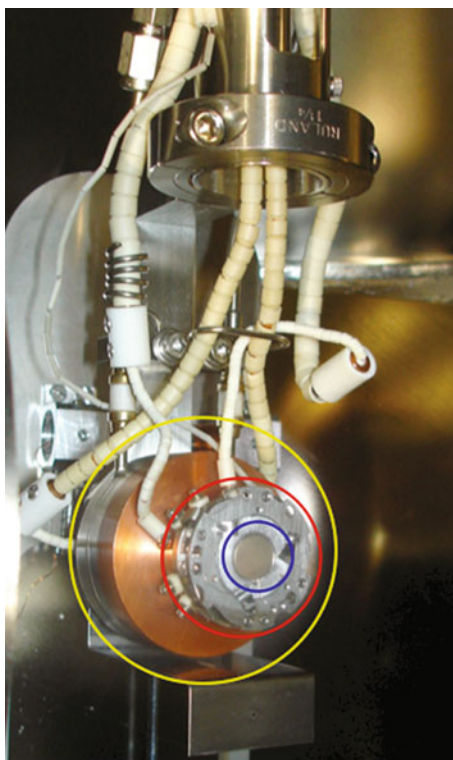


Fig. 2.1 Overall view of experimental setup

Fig. 2.2 Photo of Ni(100) surface (*encircled in blue*) mounted on sample platen (*encircled in red*) attached to XYZ sample manipulator (copper cooling block *encircled in yellow*) in the UHV chamber



We use the chopper to produce short molecular beam pulses for velocity measurements of the molecular beam by time-of-flight (TOF). A 500 l/s turbo pump (Balzers TMU520) backed by a dry membrane pump (Pfeiffer MDT4) gives a working pressure of $\sim 2 \times 10^{-5}$ mbar in the second stage. A manually operated gate-valve separates the 2nd and 3rd stages, so that the molecular beam source can be vented for servicing without breaking vacuum in the UHV chamber.

The 3rd stage serves to minimize the gas load from the source chamber into the UHV chamber. The molecular beam diameter entering the UHV chamber is defined by a removable aperture (currently $\varnothing = 1$ mm) at the exit of the 3rd stage. The 3rd stage is pumped by a 500 l/s turbo pump (Pfeiffer TMU521 P) backed by a dry membrane pump (Pfeiffer MDT4) to a working pressure of $\sim 2 \times 10^{-6}$ mbar.

2.3 Surface Science UHV Chamber

2.3.1 Overview

Our state-resolved reactivity measurements are done in a custom built Ultra-High Vacuum (UHV) surface science chamber that is pumped by a 1,000 l/s turbo pump (Pfeiffer, TMU 1000P) backed by an oil free membrane pump (KNF N920, speed 1 m³/h). Typically, the UHV chamber's base pressure is $< 5 \times 10^{-11}$ mbar, and rises to $> 1 \times 10^{-8}$ mbar when the continuous molecular beam is in use. The UHV chamber has a three-level design. The lower level contains vacuum gauges, two calibrated leaks, an electrical feed through for a pyroelectric detector, the swivel arm for a mica flag used to scatter the molecular beam during King and Wells experiments [1], and a load lock enabling us to change the single crystal sample without breaking the UHV chamber's vacuum. The middle level has the entrance aperture of the molecular beam, an entrance and exit window for the excitation laser to traverse the molecular beam, and a quadrupole mass spectrometer (Hiden, HAL 301/3FPIC) for molecular beam time-of-flight and flux measurements. The upper level is for surface cleaning and analysis. It houses a low energy electron diffraction spectrometer (LEED) (Omicron, SPECTALEED) for surface structure analysis, an Auger electron spectrometer (AES) (Omicron, CMA150) for surface composition analysis, and an ion sputter gun (Omicron, ISE10) for surface preparation.

Figure 2.2 shows a picture of a Ni-crystal mounted onto the sample manipulator in the UHV chamber. The sample surface is mounted on a four axis manipulator (Thermionics) with a 40 cm stroke (resolution = 12.7 μ m) along the vertical Z-axis, ± 20 mm displacement (resolution = 2.5 μ m) of X or Y in the horizontal plane, and 360° rotation about the Z-axis. A doubly differentially pumped rotation stage with three spring-loaded Teflon seals permits the rotation under UHV. All electrical and cooling connections to the manipulator are made through the rotating top flange to prevent in vacuum flexing of electrical wires and tubing. The

X-axis and Z-axis micrometer drives are equipped with stepper motors for automated motion of the sample via home-written Labview code. This automated motion is used to produce AES profile scans across the sample surface quantifying the amount of carbon present on the surface after a molecular beam deposition experiment.

A 10 mm diameter Ni(100) or Ni(110) single crystal is mounted on a removable sample holder (platen) that attaches to a copper dewar-heater assembly on the sample manipulator. The sample, with a K-type thermocouple is either slid into a spark eroded hole in the crystal's edge or spot-welded onto the side of a top-hat shaped crystal, can be transferred to/from the copper dewar assembly without breaking vacuum via a magnetically coupled rotary-linear feed through (Thermionics, FLRE) through a load lock chamber.

The sample is heated by electron impact and cooled by flowing liquid nitrogen through the dewar. The heating is commercially available (Thermionics, STLC-TTC platen) with power supply (SPS series) and PID controller (Omicron, E5AK). A 0.3 mm tungsten filament situated behind the crystal sample provides heat via electron bombardment. Electrons are accelerated toward the grounded sample by the negative potential (filament HV) applied to the filament (max = 2 kV). The PID controller regulates the sample temperature by 'current regulation', changing the alternating current used to heat the filament. To stabilize the crystal temperature at 200 °C, the filament HV and current are limited to -500 V and 9 A, respectively. These settings produce a temperature stability to within 1 °C. Liquid nitrogen is continuously flowed through the copper dewar assembly.

2.3.2 *Quadrupole Mass Spectrometer (QMS)*

For absolute reactivity measurements, it is necessary to determine the molecular beam's velocity/translational energy and its flux impinging on the crystal surface. We use a quadrupole mass spectrometer (Hiden, HAL 301/3FPIC) for molecular beam time-of-flight and flux measurements.

2.3.2.1 *Time-of-Flight Velocity Measurements*

The molecular beam velocity or translational energy is characterized by time-of-flight (TOF) measurements. For this, we use the chopper (located in the 2nd stage of the molecular beam source), an aperture in the UHV stage, and an on-axis QMS. The chopped molecular beam is skimmed by the aperture and continues into the ionization source of the QMS. Arrival time distributions of CH_4^+ (or CD_3H^+) ions are recorded by a multichannel scaler (Turbo-MCS, Ortec). The measured TOF data is fit by a model function based on a flux-weighted Maxwell-Boltzmann distribution of velocities convoluted with an experimentally determined chopper

Table 2.1 Expansion conditions with velocity and translational energy data for the gas mixtures used in this work

Mixture (%)	T _{nozzle} (°C)	P _{backing} (bar)	Velocity (m/sec)	E _{trans.} (kJ/mol)
100 CH ₄	50	3	1,061	9.0
100 CH ₄	200	3	1,371	15.1
25 CH ₄ in H ₂	200	3	2,056	33.9
12 CH ₄ in H ₂	50	3	2,056	33.9
12 CH ₄ in H ₂	200	3	2,471	49.0
3 CH ₄ in He	50	3	1,782	25.5
1 CH ₄ in H ₂	100	3	2,854	65.3
3.6 CD ₃ H in He	40	3	1,722	28.3
3.6 CD ₃ H in He	100	3	1,894	34.2
1.5 CD ₃ H in H ₂	50	3	2,611	65.0
1.5 CD ₃ H in H ₂	100	3	2,727	70.9
100 H ₂	50	3	2,789	7.8
100 H ₂	200	3	3,499	12.3
100 He	50	3	1,849	6.8
100 He	200	3	2,285	10.5

transmission function. Detailed description of the TOF measurement and analysis is given in the theses of Schmid [2] and Maroni [3].

Table 2.1 shows the gas mixtures used in the deposition experiments presented in this thesis. It gives CW expansion conditions with resulting molecular beam velocities and translational energies for each mixture. I have included pure beams of H₂ and He for comparison.

2.3.2.2 Molecular Beam Flux Monitor

Flux measurements of the molecular beam are taken so that we can calculate the dose of molecules impinging on the surface during a molecular beam deposition experiment. This allows for correction of dose differences in deposition experiments and for the calculation of absolute sticking coefficients or reaction probabilities.

Figure 2.3 shows a flux measurement for a deposition of CH₄ on Ni(100). In this experiment, we deposited four molecular beam footprints or “spots” on the Ni surface with a 33.9 kJ/mol molecular beam for subsequent analysis by AES. For flux monitoring of CH₄, the QMS is set to measure $m/z = 16$, averaging over a dwell time of 5–15 s for each data point (15 s dwell time for data in Fig. 2.3). In contrast to the time of flight measurements, the methane beam does not enter the ionization source directly for the flux monitoring, but is scattered by the surface sample, in order to measure the partial pressure rise of the species of interest in the UHV chamber. During molecular beam deposition experiments on a reactive surface, not all of the molecular beam flux is scattered by the surface. Some impinging molecules stick (either physisorption or chemisorption) to the surface

Fig. 2.3 Typical flux measurement during a CH_4 molecular beam deposition experiment using a 33.9 kJ/mol (12% mixture) translational energy

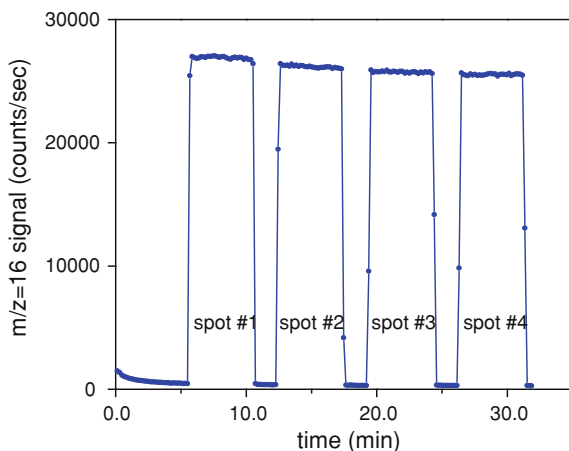
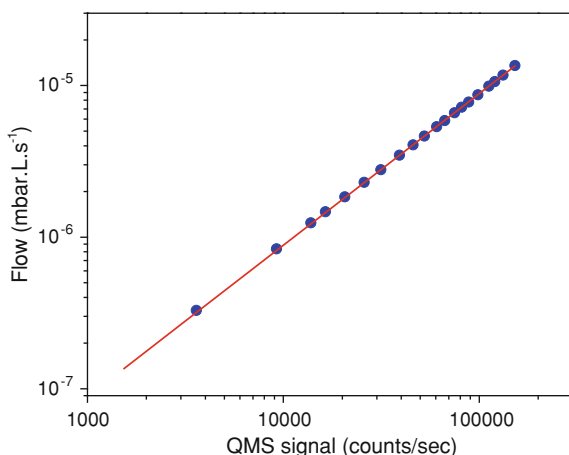


Fig. 2.4 QMS signal calibration by calibrated leak standard for CH_4 . The slope of the fitted line gives the QMS sensitivity



and cause the scattered flux to be lower than the incident. The absolute reaction (sticking) probabilities of methane reactions presented in this work are <0.005 (or less than one molecule in 200), so I take the QMS measured methane signal as the incident flux.

The QMS signal is calibrated by recording a series of steady state signals (counts/sec) for known fluxes (mbar.L/sec) introduced into the UHV by a calibrated leak standard. Figure 2.4 shows data taken to calibrate the QMS signal. From data in Fig. 2.4, we determine QMS sensitivity of 1 count/sec per 8.846×10^{-11} mbar.L/sec (2.148×10^9 molecules/sec). For a molecular beam deposition lasting 300 s (seen in Fig. 2.3) with an average QMS signal of 26,500 counts/sec, I calculate a dose of 5.69×10^{13} molecules impinging on the surface. Dividing the dose by the molecular beam's surface area ($3.14 \times 10^{-2} \text{ cm}^2$), I estimate the areal density of methane molecules that impinged on the surface during the deposition to be $1.81 \times 10^{15} \text{ molecules/cm}^2$.

Table 2.2 Observed pressure rises in the state-resolved gas/surface dynamics machine stages with measured flux for selected gas mixtures

Mixture (%)	T _{nozzle} (°C)	ΔP_{1st} (mbar)	ΔP_{2nd} (mbar)	ΔP_{3rd} (mbar)	ΔP_{UHV} (mbar)	Flux (count/sec)
100 CH ₄	200	$1.6 \cdot 10^{-3}$	$2.2 \cdot 10^{-5}$	$1.9 \cdot 10^{-6}$	$3.9 \cdot 10^{-8}$	195,000
12 CH ₄ in H ₂	50	$2.3 \cdot 10^{-3}$	$2.3 \cdot 10^{-5}$	$2.6 \cdot 10^{-6}$	$5.5 \cdot 10^{-8}$	165,000
3.6 CD ₃ H in He	40	$1.6 \cdot 10^{-4}$	$8.0 \cdot 10^{-6}$	$1.0 \cdot 10^{-6}$	$2.1 \cdot 10^{-8}$	24,500
3.6 CD ₃ H in He	100	$1.4 \cdot 10^{-4}$	$8.0 \cdot 10^{-6}$	$1.1 \cdot 10^{-6}$	$1.9 \cdot 10^{-8}$	33,000
1.5 CD ₃ H in H ₂	50	$1.6 \cdot 10^{-3}$	$2.4 \cdot 10^{-5}$	$2.6 \cdot 10^{-6a}$	$5.2 \cdot 10^{-8a}$	2,600 ^a
1.5 CD ₃ H in H ₂	100	$1.4 \cdot 10^{-3}$	$2.5 \cdot 10^{-5}$	$4.5 \cdot 10^{-7a}$	$8.2 \cdot 10^{-9a}$	2,200 ^a

^a indicates spinning of the chopper wheel located in the 2nd stage, causing 7.15x less flux to enter the 3rd and UHV stages

Table 2.2 gives typical values for the observed pressure rises in the four chambers of the machine as well as the measured flux of methane.

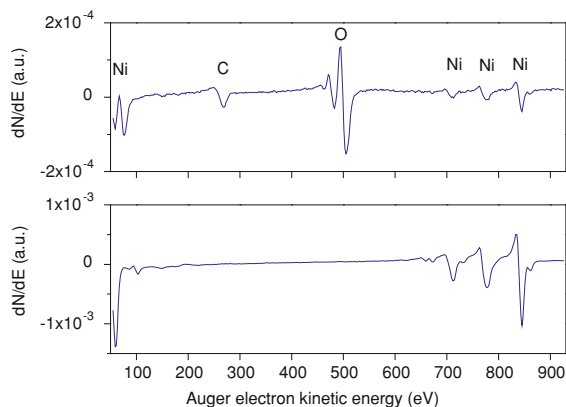
2.3.3 Sample Preparation

Before every molecular beam deposition experiment, the Ni surface must be free from contaminants (i.e. carbon, oxygen, sulfur) and have a well defined crystal structure. We clean the nickel crystal by sputtering with energetic argon ions (1 kV) from a commercial ion gun (Omicron, ISE 10). A total current leaving the gun of 20 μ A corresponds to $\sim 2 \mu$ A impinging on the 19 mm diameter crystal sample holder [2]. During the sputtering, the partial pressure of argon (PanGas, 99.999% purity) in the UHV chamber is $\sim 5 \times 10^{-7}$ mbar. Under these conditions, the ion dose on the surface after 5 min of sputtering is 1,015 ions/cm². After sputtering, the crystal structure is restored by annealing the sample for 5 min at 800 °C. The cleanliness of the sample surface is verified before every deposition experiment by AES, which is discussed in the following section.

2.3.4 Auger Spectrometer

We use an Auger spectrometer (Omicron CMA 150) with a single pass cylindrical mirror analyzer (CMA) and an integrated electron-gun (EKI 25) to assess the cleanliness of the sample surface and to quantify the amount of adsorbate (i.e. carbon) on the surface after a molecular beam deposition. Auger electron spectroscopy (AES) is a common surface science technique consisting of the detection of inelastically scattered electrons. The Auger process begins with the removal of an electron from an atom's inner shell to form a vacancy. This vacancy is filled by a second atomic electron that resided in a higher shell. As the second electron relaxes to the inner shell, energy is released. A third electron, the Auger electron, is

Fig. 2.5 Auger spectra of a Ni(110) single crystal upon introduction to UHV chamber (*upper panel*) and after a few sputtering/annealing cycles (*lower panel*)



ejected from the atom's electronic shell and carries away as kinetic energy any energy in excess to its binding energy. Since the kinetic energy of the Auger electron depends solely on the energy level spacings of the parent atom, AES is an ideal probe of the atomic composition on a surface. It is possible to detect any atomic species with AES except hydrogen and helium, as they do not have three electrons.

A detailed description of our AES setup, calibration, and procedure is outlined in the theses of Schmid [2] and, more recently, Maroni [3]. A brief description is given here. Primary electrons are produced by the electron-gun, with adjustable energy and emission current via the electron-gun controller. The Auger electrons emitted from the nickel surface are filtered in energy in the CMA. The energy of the transmitted electrons depends on the voltage applied on the cylindrical mirrors, controlled remotely via a 0–10 V digital-to-analog (DAC) of a DAQ card. The CMA controller supplies the HV (1.8 kV) for the channeltron detector. The derivative of the Auger electron current relative to the Auger electron kinetic energy is recorded by modulating the CMA HV with a sine wave (5.5 V peak-to-peak at 9.7 kHz) generated by the oscillator of a digital dual-phase lock-in amplifier (SR830). The Auger signal from the channeltron is pre-amplified (300x) and detected by the SR830 that is remotely controlled via a GPIB interface. Phase sensitive detection is employed to suppress the background signal due to elastically scattered electrons from the surface.

As mentioned in the previous section, Auger spectroscopy is used to check the cleanliness of a sample surface before a deposition experiment. The upper panel in Fig. 2.5 shows an Auger spectrum of a contaminated (dirty) Ni(110) sample upon transfer into the UHV chamber. The lower panel shows an Auger spectrum of the same sample after cleaning. Typical operating conditions for Auger spectra collection are 1 μ A of electron current, a dwell time of 20 ms, step width of 2 eV and the channeltron set to 1,800 V. Data is collected with 5.5 V modulation at 9.7 kHz, by a lock-in amplifier with sensitivity of 10 mV(nA) and time constant of 10 ms.

AES is also used to quantify the reactivity of methane in a molecular beam. The dissociative chemisorption reaction of methane on a 200 °C nickel crystal yields carbon atoms chemisorbed to the surface. Methane is completely dehydrogenated

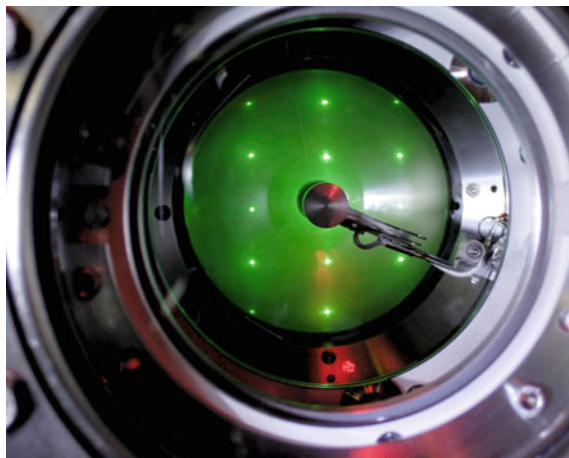


Fig. 2.6 LEED pattern of a Ni(110) single crystal

and the hydrogen leaves the surface by recombinative desorption at 200 °C surface temperature.

After an exposure to a known dose of methane in a molecular beam, the amount of carbon on the surface is quantified as the ratio between carbon and nickel peak intensities (C/Ni ratio) to compensate for variations in collection efficiencies and e-beam current. When analyzing the surface for carbon products of methane's dissociative chemisorption, AES signals are recorded in two regions. The first region of 260–290 eV is for the detection of the KLL transition of carbon, and the second region from 825 to 870 eV contains the intense LMM transition of nickel. The carbon (C) and nickel (Ni) peaks used to generate the C/Ni ratio are visible in Fig. 2.5. After calibration (discussed in Sect. 4.2.2), the C/Ni ratio produces a quantitative measure of the amount of carbon. The AES C/Ni signal is measured at several points along the surface to produce a 'profile' of the carbon 'spot' formed during the molecular beam exposure to the single crystal nickel surface. Auger 'profile' scans are used throughout this thesis.

2.3.5 LEED Spectrometer

Low energy electron diffraction (LEED) is used to obtain qualitative information about the sample's surface structure and to characterize the azimuthal orientation of the single crystal samples. The spectrometer (Omicron, SPECTALEED) has a low profile integrated electron gun. In LEED, a crystalline surface is bombarded with a collimated beam of low-energy electrons. The diffracted electrons are imaged as spots on a fluorescent screen. A LEED pattern of the Ni(110) crystal after cleaning (sputtering and annealing) is shown in Fig. 2.6. This confirms that the annealing process reconstructs the surface to its single crystal configuration.

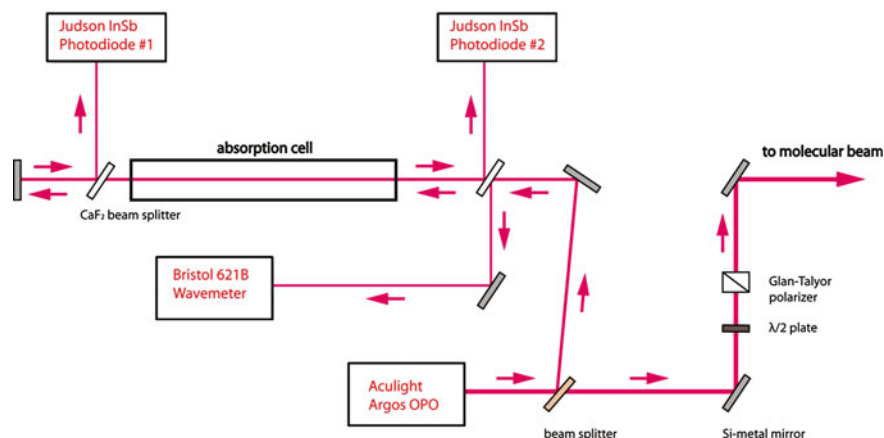


Fig. 2.7 Optical layout for the experiments conducted in this thesis work

LEED is used in [Chap. 5](#) to characterize the alignment of the surface rows of Ni(110) in the laboratory frame.

2.4 CW-IR State-Preparation Setup

During this thesis work, the experimental setup (i.e. molecular beam and optical excitation scheme) changed from ‘pulsed’ to ‘continuous’. Nevertheless, the goal of the experiment remains: quantum state-preparation of a molecular beam of methane for state-resolved gas/surface reactivity measurements, with the addition of alignment of the gas-phase reactant and the surface structure for the study of steric effects in vibrationally excited methane chemisorption. In this section, I discuss the CW-excitation scheme that has been developed during this thesis project.

2.4.1 Overview

Figure [2.7](#) presents the optical layout of our experimental setup and will be referred to throughout this section. I describe the light source (Aculight Argos OPO), the wavemeter (Bristol 621B), the tunable $\lambda/2$ wave plate (Alphas GmbH) individually in the following sections of this chapter.

Tunable, single mode infrared radiation is generated by an optical parametric oscillator (OPO) which is pumped by a fiber laser. After separation of the signal and pump radiation, we split off between 5 and 15% of the horizontally polarized idler output towards a frequency stabilization and diagnostic setup consisting of an

absorption cell, IR-photodiodes and an IR-wavemeter. The angle of this beam splitter is chosen to give a sufficient amount of power to the frequency stabilization setup to generate a Lamb dip in a 1.6 m long absorption cell, typically filled with 20–100 μbar of gas at room temperature. The two CaF_2 beam splitters are used to send light to the wavemeter and the two photodiodes used as direct absorption detectors of the light traversing the absorption cell. Photodiode #1 is used for absorption measurements after the light makes a single pass through the cell. Photodiode #2 is used for absorption measurements after the light makes a round-trip through the absorption cell. Both measurement types are discussed in this chapter.

The five mirrors used in the optical setup, represented as gray rectangles with black edges, are silver (Ag) coated silicon discs ($\varnothing = 50.8 \text{ mm}$) and have a polarization-independent reflectivity of $>96\%$ at $3.3 \mu\text{m}$. They are used to steer the laser beam into the wavemeter, through the absorption cell (back and forth), and to cross the molecular beam.

The Glan-Taylor linear polarizer in this optical setup is used in conjunction with tunable $\lambda/2$ wave plate to serve as a continuously variable power attenuator of the linearly polarized CW excitation laser. We varied the excitation laser power from $\sim 0 \text{ mW}$ (polarizer axis aligned perpendicular to the horizontal polarized OPO idler output) to $\sim 90\%$ transmission of the polarizer using the $\lambda/2$ waveplate to rotate the polarization of light incident on polarizer). For the experiments presented in this thesis, we employed a YVO_4 Glan-Taylor polarizer from AlphaLas GmbH. The YVO_4 Glan-Taylor polarizer is composed of two right-angled YVO_4 (birefringent) prisms separated by an air gap between their long faces at nearly Brewster's angle. It has a wavelength range of $500\text{--}4,000 \text{ nm}$ ($20,000\text{--}2,500 \text{ cm}^{-1}$).

2.4.2 Light Source

The light source used here is an Argos model 2400 continuous wave, single mode optical parametric oscillator (OPO) produced by the Lockheed Martin Acculight corporation [4]. Optical parametric oscillation is a parametric process in which a coherent ‘pump’ laser beam is split into two lower frequency beams, termed ‘signal’ and ‘idler’ in a crystal that has sufficiently large nonlinear susceptibility. The ‘signal’ refers to the frequency that is resonant in the OPO cavity for a singly-resonant cavity. Due to the law of the conservation of energy, the equation dictating how the ‘pump’ frequency ω_{pump} can be split into ‘signal’ ω_{signal} and ‘idler’ ω_{idler} is

$$\omega_{\text{pump}} = \omega_{\text{signal}} + \omega_{\text{idler}}. \quad (2.1)$$

The Argos 2400 mid-infrared light source offers a continuously tunable idler wavelength range from 2.3 to $3.9 \mu\text{m}$ ($4,350\text{--}2,600 \text{ cm}^{-1}$) using three different OPO modules (A from 2.3 to $2.5 \mu\text{m}$, B from 2.5 to $3.2 \mu\text{m}$ and C from 3.2 to $3.9 \mu\text{m}$). In this work we are using module ‘C’ ($3,100\text{--}2,600 \text{ cm}^{-1}$). The attractive features of the Argos model 2400 are its high power ($>1 \text{ W}$ over entire tuning

range), narrow linewidth (<1 MHz for both signal and idler), CW output, good beam quality ($M^2 < 1.1$) and linear polarization.

The OPO pump source is a continuous, 15 W, single mode, diode pumped, fiber amplifier operating at 1,064 nm and continuously tunable over 50 GHz without mode hops. It consists of a distributed feedback (DFB) Yb-doped fiber laser with a bandwidth of <100 kHz that seeds a 15 W fiber amplifier. The pump light is transmitted through an armored fiber cable to the OPO module. The pump source output is a collimator lens barrel that can be ‘keyed’ to the input of the OPO module, allowing for ‘alignment free’ pump changing between the various modules that cover the system’s frequency range. Only the signal wavelength is resonant in the OPO cavity. The idler exits the OPO after a single pass.

The nonlinear material in the OPO is a lithium niobate, LiNbO_3 (LN), crystal. The crystal is periodically-poled (PP), meaning that the birefringent material is formed with domains of alternating orientation such that the alternation period is a multiple of the desired wavelength of operation. Periodic poling is often accomplished by ‘ferroelectric domain engineering’ which uses micro-structured electrodes to apply a strong electric field to the crystal so that the crystal orientation and the sign of the nonlinear coefficient are permanently reversed under the electrodes [5]. This structured medium is used to achieve quasi-phase matching (QPM) in the material. Furthermore, the periodic poling is engineered in a ‘fan out’ pattern such that the poling period varies continuously across the LN crystal. This ‘fan out’ pattern allows for a wide tuning range of the OPO for a single PPLN crystal by translating the crystal to sample different poling periods with the pump laser.

Tuning of the OPO output wavelengths (signal and/or idler) is accomplished in three steps: coarse, intermediate and fine tuning. Course tuning ($\sim 13 \text{ cm}^{-1}$ steps as defined by the free spectral range of the etalon in the laser cavity) of the OPO signal frequency is accomplished by translation of the PP-LN crystal, changing the poling period of the LiNbO_3 exposed to the pump beam to achieve phase matching for the desired signal and idler combination. Intermediate frequency tuning of the signal is accomplished by changing the angle of an intra-cavity Fabry–Perot etalon with a free spectral range of 400 GHz (or $\sim 13 \text{ cm}^{-1}$) in the oscillator cavity via a galvanometer ($\sim 1 \text{ cm}^{-1}$ steps in signal frequency defined by the cavity mode spacing). Tilting the etalon by 2° ($\pm 1^\circ$) covers a complete free spectral range of the etalon. Fine tuning of the OPO idler frequency can be achieved by applying strain to the DFB seed laser via a piezo element with a voltage (0–90 V allows continuous tuning over 1.7 cm^{-1}) (50 GHz). Straining the DFB seed laser causes a frequency change in the pump laser and therefore in the idler output since the resonant signal frequency is fixed by the OPO cavity. This is due to Eq. 2.1.

Figures 2.8a and b show the idler intensity profile in the horizontal and vertical direction as a function of distance from the OPO’s output. This data was collected by a model TS50 infrared camera from ThermoSENSORIK GmbH.

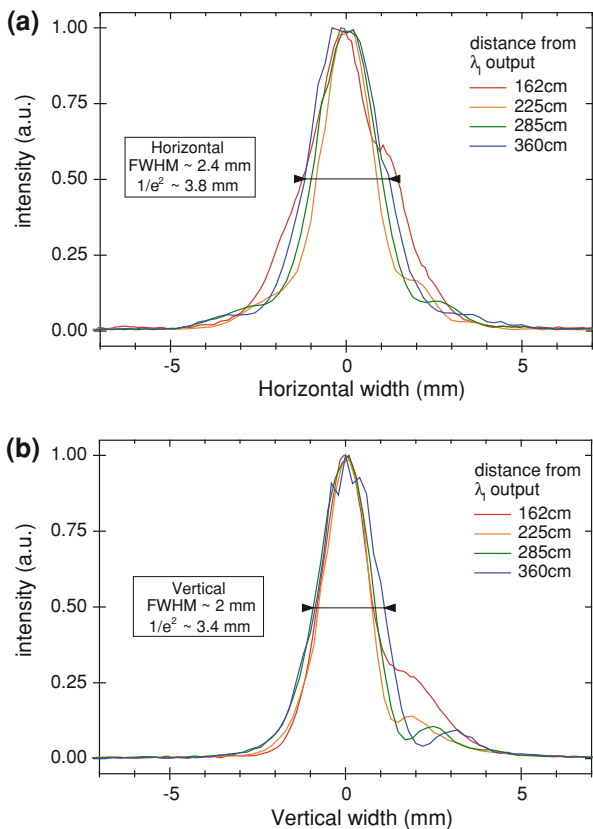
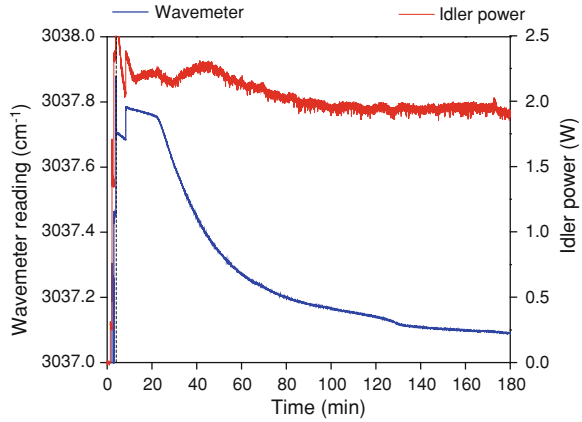


Fig. 2.8 **a** OPO idler beam profile (*horizontal*) as a function of distance. **b** OPO idler beam profile (*vertical*) as a function of distance

2.4.3 Wavemeter

A Bristol Instruments model 621B Laser Wavemeter is used to measure the frequency of the excitation laser. The wavemeter has a specified wavelength range of 1.0–5.0 μm , an absolute accuracy of $\pm 0.0023 \text{ cm}^{-1}$ ($\pm 70 \text{ MHz}$) and a repeatability of $\pm 10 \text{ MHz}$ (standard deviation for a 5 min measurement) at $3,000 \text{ cm}^{-1}$. Typically, less than 1 mW of idler power is needed for frequency characterization. As shown in Fig. 2.7, the light used for the wavemeter reading is split from the excitation laser beam directly before it enters into the absorption cell. As discussed in Sect. 2.5, we stabilize the laser frequency to better than the repeatability limit of the wavemeter. Therefore, the wavemeter is a useful tool to bring the excitation frequency close to the ro-vibrational transition of interest, but can not give an exact measurement of the laser's frequency stability when

Fig. 2.9 Data showing the idler frequency and power stability of the OPO as function of time



we are locked to a narrow spectral feature such as a Lamb dip with a typical full width at half maximum (FWHM) of <2 MHz.

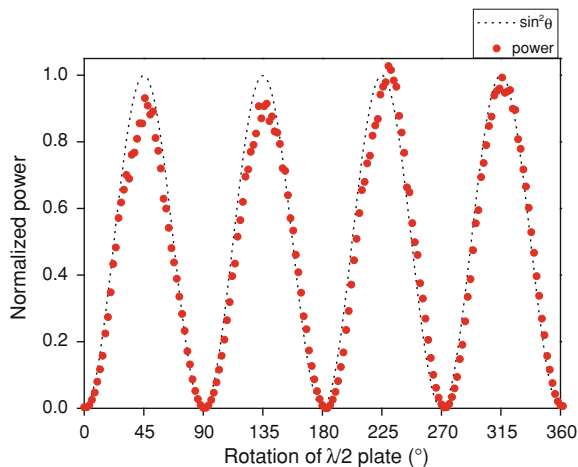
Figure 2.9 shows frequency data collected by the wavemeter as a function of time with zero-time corresponding to the OPO pump laser being turned ON. The frequency instabilities during the first 3 min in both idler power and wavemeter reading are due to the pump power being increased from 0 to 15 W in increments of 3 W. The idler frequency drifts from $3,037.8 \text{ cm}^{-1}$ to $3,037.25 \text{ cm}^{-1}$ during the first 60 min of operation at 15 W pumping. This corresponds to a frequency drift of $\sim 16.5 \text{ GHz}$ ($\sim 275 \text{ MHz/min}$) which makes locking of the laser frequency to ~ 1 MHz a challenge during the warmup period. However, from the 60th to the 180th minute the frequency drifts smoothly from $3,037.25 \text{ cm}^{-1}$ to $3,037.1 \text{ cm}^{-1}$ or $\sim 4.5 \text{ GHz}$ ($\sim 38 \text{ MHz/min}$). A frequency drift of this magnitude can be counteracted by changing the seed laser frequency in order to maintain the frequency ‘locked’ to <1 MHz for several hours. The frequency stabilization technique is described in the following section. Before attempting to actively stabilize the OPO idler frequency, we typically allow the laser system (the OPO pump) to warm up for ~ 1 h.

As shown in Fig. 2.9, the idler power drops from 2.37 W to 2.13 W or $\sim 11\%$ during the first 60 min of operation at 15 W pump power. From the 120th to the 180th minute, the OPO idler power decreases from 1.96 to 1.89 W or $\sim 3.5\%$. This laser (idler) power data was collected using a calibrated photodiode, and is offered as a demonstration of the stability of the OPO over an extended period of time.

2.4.4 Tunable $\lambda/2$ Wave Plate

The tunable $\lambda/2$ wave plate (Alphaslabs GmbH) in the optical setup serves two purposes: (1) In combination with a polarizer, it acts as a continuously variable power attenuator for the collection of excitation fluence dependence curves of the

Fig. 2.10 Normalized idler power transmitted through a vertical, linear polarizer as a function of $\lambda/2$ waveplate angle



molecular beam absorption and (2) it is used to rotate the polarization direction of the excitation beam which controls the alignment of the ro-vibrationally excited molecules in the molecular beam.

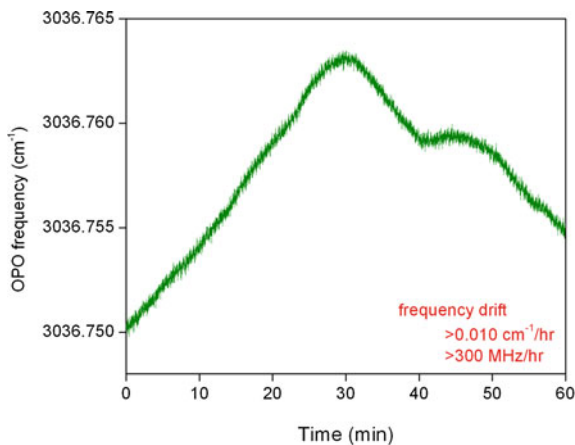
Figure 2.10 shows the idler power transmitted through a linear polarizer (aligned vertically in the laboratory frame) as a function of $\lambda/2$ plate angle. The maximum power is for vertically polarized radiation, while the minimum corresponds to horizontally polarized radiation. The extinction ratio is measured to be $<0.6\%$, confirming that the laser polarization is well defined.

2.5 Frequency Stabilization

The goal of the optical setup is to prepare a molecular beam of methane in a specific quantum state. For example, we want to excite CH_4 with one quantum of the antisymmetric stretch (ν_3) of CH_4 with a band origin at 3018.825 cm^{-1} and the CH-stretch (ν_1) of CD_3H with a band origin at 2992.745 cm^{-1} . For reliable excitation of rovibrational transitions in the molecular beam, the frequency of the excitation laser needs to be stable to within the homogeneous linewidth of the transition in the molecular beam. For our experimental conditions, transit time broadening dictates the absorption linewidth to be $\sim 1 \text{ MHz}$ [6]. This frequency stability is needed on the time scale of minutes to hours for our quantum state-prepared molecular beam deposition experiments.

The OPO pump laser is sensitive to temperature fluctuations and air currents in the laboratory. Its frequency can drift several MHz on the minute time scale and hundreds of MHz in an hour. Figure 2.11 shows the inherent frequency stability of the OPO output is not sufficient to maintain resonance with a given transition in the molecular beam of $\sim 1 \text{ MHz}$ (FWHM). The data in Fig. 2.11 was collected at

Fig. 2.11 Data taken for 1 h (after 3 h at 12 W pump power) to demonstrate the inherent frequency stability of OPO idler output



a frequency of 1 Hz with the Bristol Instruments wavemeter in our optical setup, see Fig. 2.7.

Since the OPO frequency is not inherently stable to 1 MHz, even on the second time scale, a way to stabilize or ‘lock’ the frequency of the OPO resonant to a rovibrational transition in the molecular beam is needed. This can be accomplished by a feedback control loop. The reference signal of the control loop must be well defined at the rovibrational transition frequency and be ‘signed’. By ‘signed’, I mean that if the laser frequency drifts off-resonance, the reference signal should contain information as to the drift direction. We have chosen to actively stabilize the excitation laser frequency to the first derivative of a Lamb dip generated in a Doppler broadened transition [7]. The signal generation and utility is explained in this section.

To bring the laser frequency into resonance with and actively stabilize it to a rovibrational transition, we can use an absorption cell filled with the gas of interest, see Fig. 2.7. The laser frequency is modulated about a rovibrational transition of the gas in the cell. After the excitation laser makes a single pass through the absorption cell, the absorption of light due to the Doppler broadened transition in the room temperature cell can be detected with a photodiode #1, as depicted in Fig. 2.12(left).

Phase sensitive detection of the absorption signal by a lock-in amplifier produces the first derivative (derivative) of the Doppler broadened transition, as depicted in Fig. 2.12(right). The ‘derivative’ is generated by multiplying the absorption signal (signal) by the modulation (reference) and averaging the result by a low pass filter. The zero crossing of the ‘derivative’ represents a maximum (or minimum) in the signal. Furthermore, the ‘derivative’ contains information for the direction of the corrective response as its sign is dependent on frequency drift direction. The derivative signal can be processed by a regulator circuit to generate a control signal to be feedback to the frequency determining element of the excitation laser. Via this control loop, the laser frequency can be stabilized to

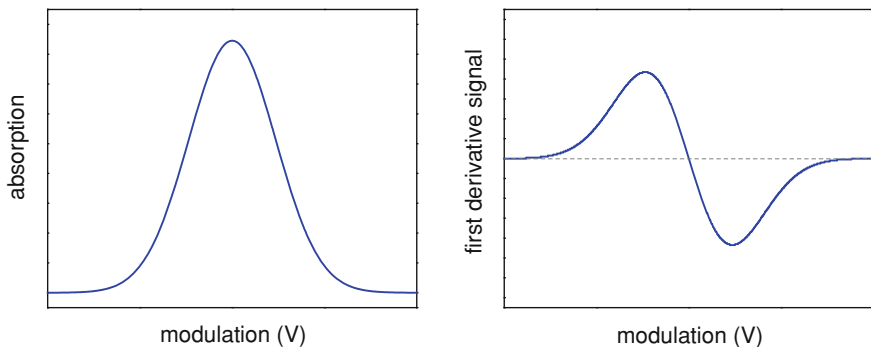


Fig. 2.12 Simulated Doppler broadened absorption signal (*left*) and its first derivative signal (*right*) as a function of a modulation voltage that dictates the frequency of the excitation laser

the maximum of the Doppler broadened transition by actively stabilizing the absorption's derivative signal to its zero crossing.

The only problem with frequency stabilization to the maximum of the Doppler broadened transition is the achievable frequency definition. A typical Doppler broadened linewidth for methane excited with 3 μm light in a room temperature gas is ~ 300 MHz (FWHM). As stated above, we need to stabilize the laser frequency to ~ 1 MHz in order to maintain resonance with a transition in the molecular beam. Frequency stabilization to a ~ 300 MHz absorption line will not fulfill this requirement.

Retroreflection of the excitation laser produces a saturation dip in the center of the Doppler broadened absorption signal. This well known spectral feature [8–11] is called a Lamb dip, after the American physicist Willis Eugene Lamb. When the excitation laser frequency is slightly detuned from the Doppler broadened (transition), the counterpropagating laser beams interact with different subgroups of the velocity distribution characterized by Doppler shifts ($\Delta\omega_B$) from

$$\Delta\omega_B = \omega_B v_z / c. \quad (2.2)$$

Here, v_z is the velocity component along the laser propagation axis, ω_B is the transition's center or Bohr frequency, and c is the speed of light. As the excitation laser frequency approaches ω_B , the counterpropagating laser beams compete to excite the same Doppler sub-set of molecules, namely those molecules with no velocity along the propagation axis of the excitation laser. This competition leads to a decrease in the absorption signal if the laser power is sufficiently high to saturate the transition.

Figure 2.13(left) shows a simulated Lamb dip in a Doppler broadened absorption. With phase sensitive detection, a steep zero crossing corresponding to the Lamb dip minimum is observed. The first derivative of a Lamb dip signal is depicted in Fig. 2.13(right). Typical Lamb dip linewidths are in the vicinity of

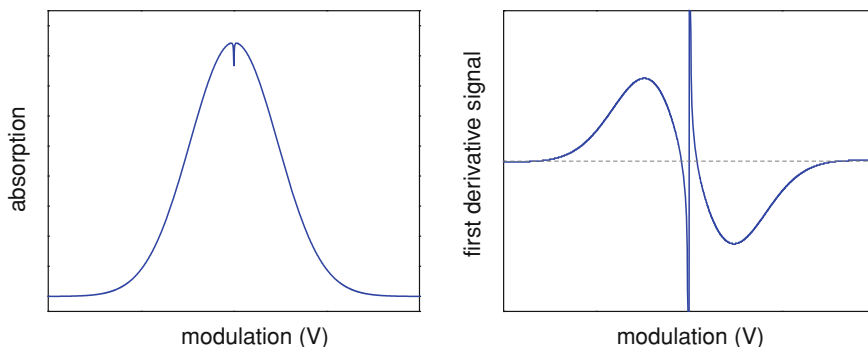


Fig. 2.13 Simulated Lamb dip in Doppler broadened absorption signal (*left*) and its first derivative signal (*right*) as a function of a modulation voltage that dictates the frequency of the excitation laser

1 MHz and allow for a much higher definition of the laser frequency than the Doppler broadened transition would.

The Lamb dip signal corresponds precisely to the zero-Doppler shifted molecular absorption frequency, which is the needed frequency for excitation of the molecular beam. The center-line trajectory of a molecular beam has a zero-Doppler shifted absorption when the excitation crosses at a right angle to it (as we do).

2.5.1 Lamb Dip Detection and Characterization

Below, I discuss the details of the excitation laser frequency stabilization. Typically, Lamb dip spectra are generated with the absorption cell filled to a pressure of 20–30 μbar for $\text{CH}_4(\nu_3)$ or 80–100 μbar for $\text{CD}_3\text{H}(\nu_1)$.

The Doppler broadened absorption profile of $\text{CH}_4(\nu_3)\text{-R}(0)$ shown in Fig. 2.14 was recorded by sending a single pass of 8 mW of the OPO idler through the absorption cell, filled with 30 μbar of CH_4 . The OPO idler frequency was modulated by ‘scanning’ the voltage applied to the OPO pump’s seed laser with an 8 V amplitude, 10 Hz triangle waveform. The transmitted idler intensity was detected by photodiode #1, (see Fig. 2.7) connected to the analog/digital converter input of a 12-bit National Instruments model 6023-E data acquisition card (DAQ) at a sampling rate of 100,000 samples/sec. The spectrum consists of 5,000 points.

A Gaussian fit of the measured absorption line is shown in Fig. 2.17. At the absorption peak, the absorption cell transmission was 46% which corresponds to an absorbance of 0.78. I calibrated the frequency scale of the OPO idler using the calculated 278.3 MHz linewidth of the Doppler broadened $\text{CH}_4(\nu_3)\text{-R}(0)$ line ($3028.75218\text{ cm}^{-1}$) [12] at room temperature and the FWHM of the Gaussian fit of 1,383 samples (data points). This gave a calibration of 4.97 samples/MHz (or $1,383/278.3$ samples/MHz) for these specific experimental conditions.

Fig. 2.14 Characteristic Doppler broadened $\text{CH}_4(\nu_3)$ -R(0) transition at room temperature. $P_{\text{cell}} = 30 \mu\text{bar}$, $P_{\text{idler}} = 8 \text{ mW}$, OPO frequency modulation by an 8 V amplitude triangle wave at 10 Hz. The photodiode baseline is shown to display the raw data used to determine cell transmission

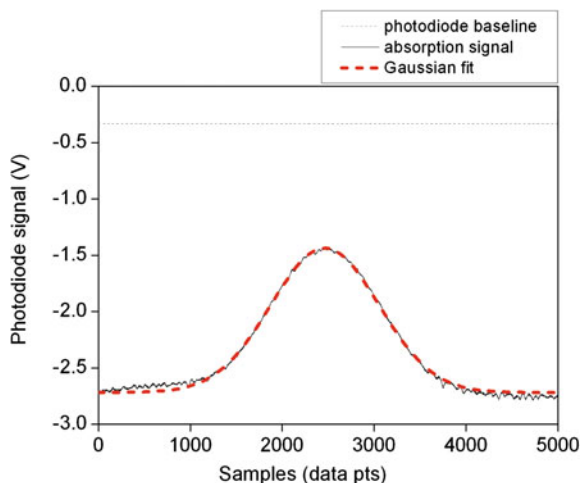
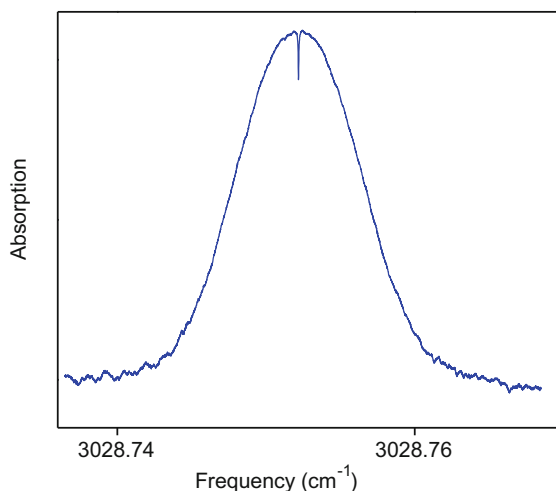


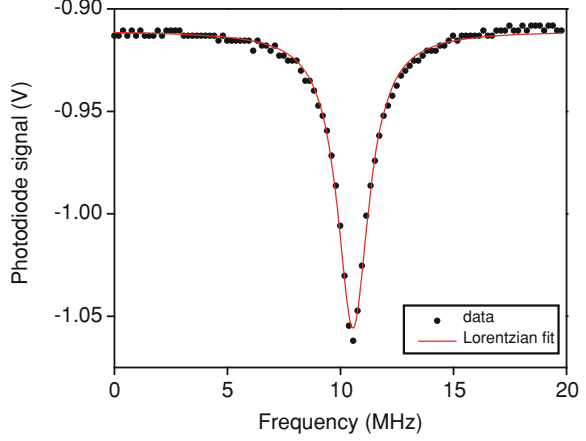
Fig. 2.15 Doppler-free saturation Lamb dip within a Doppler broadened $\text{CH}_4(\nu_3)$ -R(0) transition at room temperature. $P_{\text{cell}} = 30 \mu\text{bar}$, $P_{\text{idler}} = 85 \text{ mW}$, modulation by an 8 V amplitude triangle wave at 10 Hz



Under the same experimental modulation conditions as the calibration described above, I produced a saturation (Lamb) dip in the $\text{CH}_4(\nu_3)$ -R(0) Doppler broadened absorption profile. Figure 2.15 shows an absorption profile that was recorded with photodiode #2 (see Fig. 2.7) after the excitation beam was retroreflected through the cell. In Fig. 2.15, the x-axis is displayed in cm^{-1} using the known absorption line center for $\text{CH}_4(\nu_3)$ -R(0) and the 4.97 samples/MHz calibration from above.

The Lamb dip shown in Fig. 2.15 has a ‘contrast ratio’ (intensity ratio of the Lamb dip to its Doppler broadened absorption) of 13%. This sharp, Doppler-free spectral feature is important, since we stabilize the excitation beam’s frequency to it. The infrared absorption of methane in the molecular beam is homogeneously

Fig. 2.16 Zoomed view of Lamb dip in previous figure. FWHM determined to be 1.76 MHz from this Lorentzian fit. From repeated measurements, the FWHM of a Lamb dip in $\text{CH}_4(\nu_3)$ using 30 mbar of in the cell and a power of 85 mW at its input is found to be 1.52 ± 0.27 MHz



broadened to approximately 1 MHz. To maintain the excitation laser resonant with a molecular beam transition, it is necessary to define the laser frequency to better than the linewidth of the transition in the molecular beam.

I measured the Lamb dip linewidth on three separate days and determined its FWHM to be 1.52 ± 0.27 MHz for the $\text{CH}_4(\nu_3)$ excited via the $\text{R}(0)$ transition with 30 μbar of CH_4 in the room-temperature cell and 85 mW idler power at the cell input. Figure 2.16 shows a zoomed-in view of the Lamb dip of Fig. 2.15, using a relative MHz scale as the X-axis for clarity. Fitting the Lamb dip feature with a Lorentzian profile, I determined the linewidth (FWHM) of the Lamb dip to be 1.76 MHz for this spectrum.

Lamb dips in $\text{CH}_4(\nu_3)$ transitions have been reported in literature [10, 11, 13, 14]. I follow the linewidth calculations in Ref. [10] to determine the expected linewidth of the Lamb dip under our experimental conditions. The linewidth of a Doppler-free Lamb dip is determined by:
pressure broadening

$$\Delta_{\text{pressure}} = \frac{\partial \Delta_{\text{pressure}}}{\partial p} p, \quad (2.3)$$

transit-time broadening,

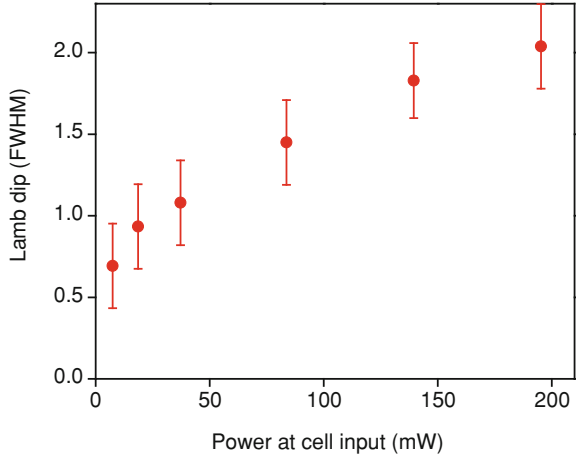
$$\Delta_{\text{transit}} = \frac{1}{4\omega_B} \sqrt{\frac{2k_B T}{m}} \quad (2.4)$$

and power broadening

$$\Delta_{\text{power}} = \Omega. \quad (2.5)$$

In the above equations, p is the gas pressure in the absorption cell, ω_0 is the excitation beam radius, k_B is the Boltzmann constant, T is temperature, m is the mass of the absorbing molecule, Ω is the Rabi frequency [15, 16].

Fig. 2.17 Study of $\text{CH}_4(\nu_3)$ -R(0) Lamb dip linewidth as a function of excitation laser power for cell. *Error bars* represent the standard deviation of repeated measurements at laser power of 85 mW at the cell input. $P_{\text{cell}} = 30 \mu\text{bar}$



Using a pressure-broadening coefficient of $\Delta_{\text{pressure}} = 5.1 \text{ kHz}/\mu\text{bar}$ [17], a broadening of 153 kHz (FWHM) due to a pressure of 30 μbar in the absorption cell is expected.

Using an average beam radius of 1.5 mm ($\frac{1}{e^2}$) and a temperature of 295 K, transit time broadening is expected to be 185 kHz (FWHM) for CH_4 (mass of 16 amu).

To calculate expected power broadening, we must calculate Ω . Where,

$$\Omega = \frac{\mu_{21} \cdot E}{\hbar} \quad (2.6)$$

and

$$E = \sqrt{\frac{2I}{\epsilon_0 c}} \quad (2.7)$$

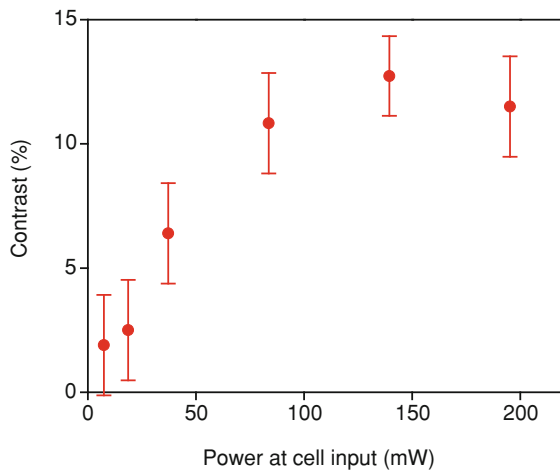
and

$$I = \frac{P}{A}. \quad (2.8)$$

Here, μ_{21} is the vibrational transition dipole moment ($1.80 \times 10^{-31} \text{ C.m}$ for $\text{CH}_4(\nu_3)$) [12], E is the electric field strength, I is the electric field intensity and is calculated simply dividing the laser power P by its area A (using the $\frac{1}{e^2}$ width of 3 mm as a diameter). I find that $I = 19.8 \text{ kW/m}^2$ and $E = 3.86 \text{ kV/m}$. This results in $\Omega = 0.82 \text{ MHz}$ which means 0.82 MHz of power broadening is expected when using an excitation power 85 mW.

I find that the dominant broadening mechanism in the experimental setup is power broadening. Figure 2.17 shows experimentally observed $\text{CH}_4(\nu_3)$ -R(0) Lamb dip linewidths (FWHM) as a function of excitation laser power at the absorption cell

Fig. 2.18 Study of $\text{CH}_4(\nu_3)\text{-R}(0)$ Lamb dip contrast ratio as a function of excitation laser power. *Error bars* represent the standard deviation of repeated measurements at laser power of 85 mW at the cell input. $P_{\text{cell}} = 30 \mu\text{bar}$



input. The data were taken with 30 μbar of CH_4 in the absorption cell, frequency modulating the OPO idler at 10 Hz with an 8 V amplitude triangle wave and collection data at 100,000 samples/sec (spectra consisting of 5,000 points).

Figure 2.18 shows the experimentally observed Lamb dip ‘contrast ratio’, or the Lamb dip’s amplitude as a percentage of the peak absorption of the Doppler broadened transition.

I typically use between 40 and 200 mW of OPO idler power to produce a Lamb dip used for active stabilization of the OPO idler frequency (<100 mW for CH_4 , >100 mW for CD_3H). For $\text{CH}_4(\nu_3)\text{-R}(0)$, this gives a Lamb dip FWHM of 1–2 MHz and a contrast ratio of 6.5–12.5%. In the following section, I discuss the same case presented in this section of 85 mW of OPO idler power for Lamb dip stabilization.

2.5.2 Lamb Dip Locking

To maintain the OPO output frequency locked to a rovibrational transition of methane for an extended amount of time, the OPO frequency (0–2 MHz) is dithered by sending a small amplitude (0–13 mV peak-to-peak) sine wave to the OPO pump’s seed laser. Then, the Lamb dip absorption signal is collected via a Judson (J10D-M204-R01 M-30) liquid nitrogen cooled photodiode with PA-7-60 pre-amplifier, and used as the AC-coupled amplifier output with a gain of 2.5×10^4 as the input of the LaseLock 3.0 Universal Laser Stabilization Electronics.

Frequency stabilization is done with the LaseLock 3.0 Universal Laser Stabilization Electronics produced by TEM Messtechnik GmbH. Figure 2.19 shows a schematic of the device. The LaseLock 3.0 is composed of:

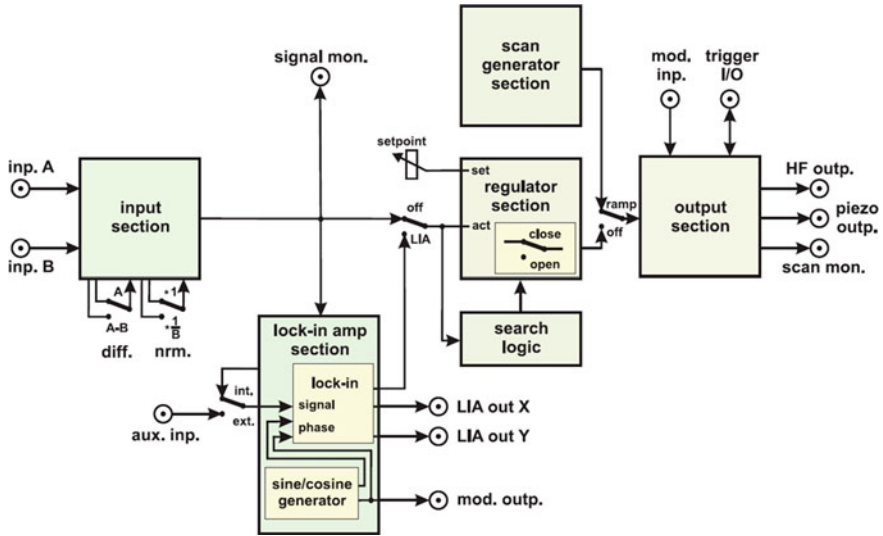
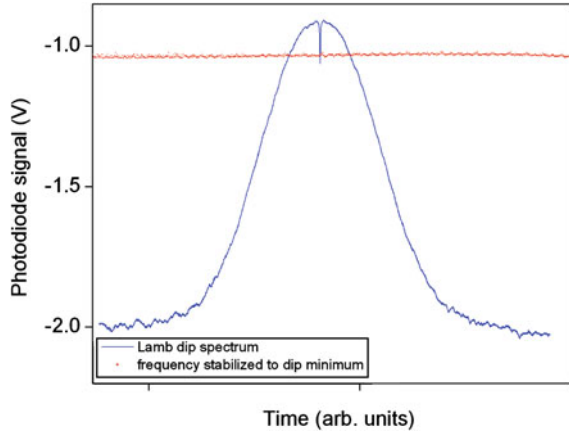


Fig. 2.19 Schematic of the LaseLock 3.0 (TEM Messtechnik GmbH). Figure is reproduced with permission

1. input amplifier
2. lock-in amplifier
3. 2 independent PID regulators
4. scan generator (0 to ± 10 V triangle wave)
5. voltage output (0–90 V DC).

The voltage output of the LaseLock 3.0 is connected to the piezo element of the OPO pump seed laser, so that a voltage sent from the LaseLock 3.0 corresponds to a frequency shift in the OPO's pump and, in turn, idler frequency as the signal frequency is fixed due to its oscillation in the OPO cavity. There are three ways of changing the voltage output of the LaseLock 3.0 (i.e. the OPO idler output frequency). The first is a DC offset (0–90 V) (via 'piezo outp.') that is controlled manually with a knob on the device's front panel. This allows one to tune close to the frequencies of rovibrational transitions in the absorption cell. From the Argos 2400 manual, we expect a frequency shift of 50 GHz for a 0–90 V DC variation. Another way of varying the output voltage (OPO idler frequency) is by a 'scan generator' that produces a triangle waveform (0 to ± 10 V) (via 'piezo outp.') which is useful for viewing a Doppler broadened transition and diagnosing the optical setup (i.e. alignment of counter-propagating laser beams). The third way to vary the output voltage (OPO idler frequency) is by producing a sine wave (via 'mod. outp.') with the lock-in amplifier section of the LaseLock 3.0. The sine wave modulation (0–13 mV) is used to periodically dither the idler frequency about the Lamb dip minimum so that the lock-in amplifier has a referenced signal for differentiation.

Fig. 2.20 Example photodiode signal for frequency stabilized OPO. Stabilized signal modulated at ~ 500 Hz with <1 mV amplitude sine wave. The Lamb dip was produced in Doppler broadened $\text{CH}_4(\nu_3)$ -R(0) transition at room temperature. $P_{\text{cell}} = 30$ μbar , $P_{\text{idler}} = 85$ mW, modulation by an 8 V amplitude triangle wave at 10 Hz



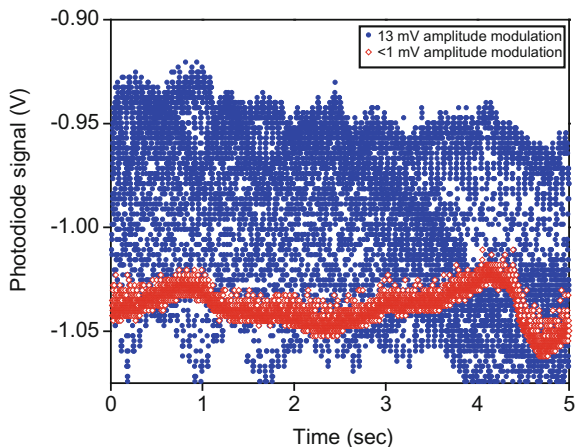
We stabilize the OPO idler frequency to the Lamb dip minimum by modulating the OPO pump laser's frequency on the Lamb dip feature with a 0–13 mV amplitude sine wave which corresponds practically to 0–2 MHz frequency modulation. The photodiode signal ('inp. A' in Fig. 2.19) of the Lamb dip is multiplied with the modulation signal, and then averaged by a low pass filter. The resulting waveform (lock-in signal) is the first derivative of the Lamb dip with respect to the OPO idler frequency, analogous to the derivative signal in Fig. 2.13 (right).

The zero-crossing of the derivative signal represents the minimum of the Lamb dip which is the excitation line center. To stabilize the OPO idler frequency, the derivative signal is processed by a Proportional-Integral-Differential (PID) regulator ('regulator section' block in Fig. 2.19) which generates a control signal that is fed back to the piezo element allowing fine tuning of the OPO pump seed and in turn the idler frequency. This closes the control loop and actively locks the idler's output frequency. A more detailed description of the frequency locking procedure and optimized settings for the LaseLock 3.0's lock-in amplifier and PID regulator are given in Appendix A.

Figure 2.20 shows two traces. The first trace is a Lamb dip spectrum of the $\text{CH}_4(\nu_3)$ -R(0) line collected with photodiode #2. The second trace is the signal collected with the same photodiode when the OPO frequency is actively stabilized to the Lamb dip minimum. The fact that the diode signal stays constant at a voltage level which corresponds to the minimum of the Lamb dip demonstrates that the idler frequency of the OPO remains stable on the Lamb dip minimum. Any instability of the idler frequency would be detected as significant amplitude noise in the photodiode signal.

Figure 2.21 shows the effect that decreasing the sine wave modulation (from 13 mV to $<<1$ mV) has on the Lamb dip signal seen by photodiode #2. The full Lamb dip height was from -0.911 to -1.056 V ($\Delta_{\text{Full}} = 145$ mV). I locked the excitation laser frequency loosely (with a sine wave modulation of 13 mV) to

Fig. 2.21 Demonstration of frequency locking to Lamb dip. The Lamb dip was produced in Doppler broadened $\text{CH}_4(v_3)\text{-R}(0)$ transition at room temperature. $P_{\text{cell}} = 30 \mu\text{bar}$, $P_{\text{idler}} = 85 \text{ mW}$



produce an absorption signal varying between -0.920 V and -1.086 V ($\Delta_{\text{Loose}} = 166.0 \text{ mV}$) with an average value $\Delta_{\text{Loose}}^{\text{Average}}$ of -0.994 ± 0.040 for a 5 s measurement collected at 1 sample/msec. Under tight locking conditions (modulation $\ll 1 \text{ mV}$), the signal varied between -1.011 and -1.062 V ($\Delta_{\text{Tight}}^{\text{Total}} = 51 \text{ mV}$) with an average value $\Delta_{\text{Tight}}^{\text{Average}}$ of $-1.038 \pm 0.008 \text{ V}$ for a 5 s measurement.

The photodiode output voltage is sensitive to the absorption signal and therefore gives a measure of the Lamb dip linewidth, but the photodiode is also sensitive to vibrations on the optical table and any variation in the excitation laser power. Therefore, any linewidth determination from the photodiode signal voltage is an upper limit (conservative estimate) to the true linewidth achieved in our experimental setup.

For the idler's linewidth determination in the 'tightly' locked configuration, I used Δ_{Full} and the average of a 5 s signal as described above. The tightly locked configuration's variation $\Delta_{\text{Tight}}^{\text{Average}}$ lies at 12.4% of the Lamb dip's full depth. Figure 2.22 shows the Lorentzian fit (FWHM = 1.76 MHz) of the data from Fig. 2.16. The full-width at 87.6% maximum (100–12.4%) gives a linewidth of $650 \pm 180 \text{ kHz}$ for the 5 s measurement. Using $\Delta_{\text{Tight}}^{\text{Total}}$, the total photodiode signal variation for the 5 s measurement, the total frequency variation for the 5 s measurement is 1.28 MHz. The 1.28 MHz is taken from the full-width at 65% of the dip minimum, since $\Delta_{\text{Tight}}^{\text{Total}}/\Delta_{\text{Full}} = 0.35$. Again, this determination is a conservative estimate of the linewidth of the actively stabilized laser frequency.

I display the long term stability achieved by the frequency locking technique with wavemeter data. Fig. 2.23 shows the wavemeter reading as a function of time after the laser system was running at a pump power of 10.5 W for an hour. For the first 38 min of the measurement, the stabilization is not used (Not Locked). During that time, the frequency drifts 0.04 cm^{-1} or 1,200 MHz. Then, the laser frequency is

Fig. 2.22 Simulated $\text{CH}_4(\nu_3)$ -R(0) Lamb dip with Lorentzian profile to illustrate frequency locking ability

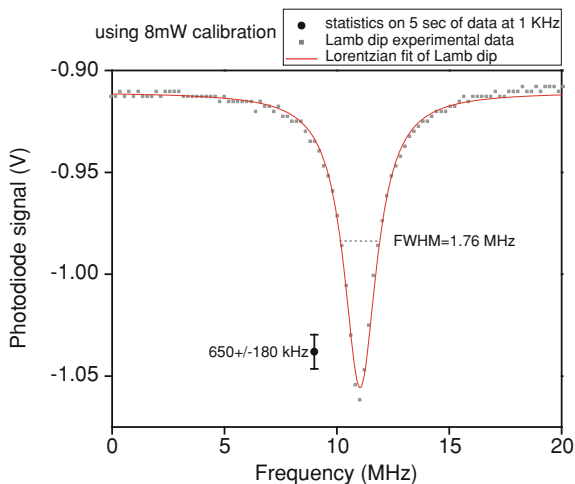
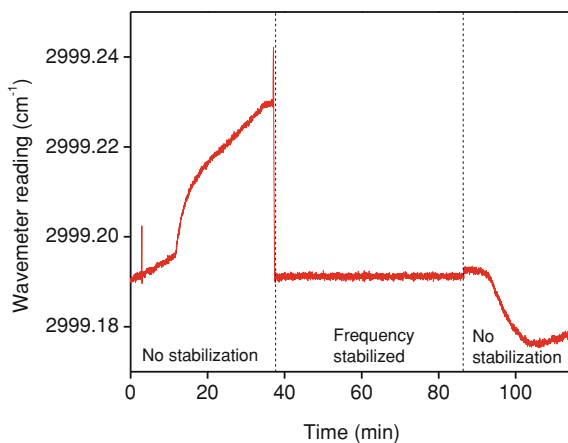


Fig. 2.23 OPO idler frequency with and without active stabilization to $\text{CD}_3\text{H}(\nu_1)$ -R(0) Lamb dip as measured by the Bristol 621B wavemeter



actively stabilized to a Lamb dip produced in the absorption cell. For this data, I stabilized the laser frequency to the R(0) transition of $\text{CD}_3\text{H}(\nu_1)$ using 190 mW of idler output from the OPO and a pressure of 80 μbar in the cell. I calculated the absorption line to be at $2999.1928 \text{ cm}^{-1}$ (see Appendix C) and measured it to be at $2999.1912 \pm 0.0004 \text{ cm}^{-1}$ ($\pm 11 \text{ MHz}$) over the 48 min that the laser was stabilized to the Lamb dip. Both the absolute accuracy and the repeatability of the wavemeter reading are within the specifications of the wavemeter, as stated in [Sect. 2.4.3](#).

The data in this section show that the excitation laser is actively stabilized to a rovibrational transition in methane via Lamb dip locking to $<1.2 \text{ MHz}$ on a 5 s timescale and maintains the locking on the hour timescale. In the following section, I characterize the excitation of the molecular beam.

2.6 Pyroelectric Detection of Vibrationally Excited Molecules in a Molecular Beam

To monitor the IR-absorption of methane and the extent of rovibrational excitation in the molecular beam, we use a pyroelectric detector. Pyroelectric detectors use the pyroelectric property of certain crystals to respond to a temperature change with an electric potential difference. Pyroelectric crystals can be thought of as possessing a permanent electric polarization. When the crystal is at a constant temperature, this polarization is compensated by free charge carriers that reach its surface by conduction through the crystal and from the surroundings. If the crystal experiences a change in temperature, the atoms in the crystal lattice modify their position which changes the permanent electric polarization of the crystal and manifests itself as pyroelectricity. The polarization potential is temporary, only present while the temperature is changing.

A pyroelectric detector responds to temperature changes and therefore is well suited for the detection of modulated signals. This lends itself to phase-sensitive detection by a lock-in amplifier. We impinge a continuous molecular beam onto a pyroelectric detector, exciting the molecular beam with a periodically chopped laser excitation. The signal on the pyroelectric detector is due to a change in the vibrational energy content in the molecular beam (excitation ON/OFF) and can be lock-in detected using the optical chopper frequency as a reference. The details of this setup are given below.

An ELTEC 406 M pyroelectric detector with a 2 mm dia. active area on a rotating arm was installed in the UHV system mounted such that the pyroelectric detector is able to be positioned into the molecular beam path.

Figure 2.24 is a photo of the interior of the UHV chamber, and shows the experimental configuration for impinging the molecular beam onto the pyroelectric detector. The molecular beam enters the UHV chamber through a 1 mm aperture, blue (upper-left) circle. The pyroelectric detector, red (upper-right) circle, is positioned in the molecular beam path by a rotation-translation feed through (yellow or lower circle) which permits positioning in two dimensions perpendicular to the molecular beam.

As the pyroelectric detector is sensitive only to changes in temperature, a continuous molecular beam will not generate a signal, after the pyroelectric detector's initial warming up from the translational energy deposited on the detector by the molecular beam. Figure 2.25 shows the signal registered by a 34 kJ/mol translational energy molecular beam of CH_4 in H_2 on the pyroelectric detector after an amplification of 10x by a home-built amplifier (design from ELTECdata 136, ELTEC Instruments, Inc.) that has variable gain of 10x and 95x. The initial voltage rise is the introduction of the molecular beam into the UHV and onto the pyroelectric detector that is positioned in the molecular beam's path. Approximately 300 ms after the CW molecular beam begins to impinge on the pyroelectric detector, the detector reaches its peak voltage. Approximately 8 s

Fig. 2.24 Photo of pyroelectric detector (*red circle*) positioned in molecular beam path (whose input aperture to the UHV, *blue circle*) by rotation of swivel arm (*yellow circle*) in the UHV chamber

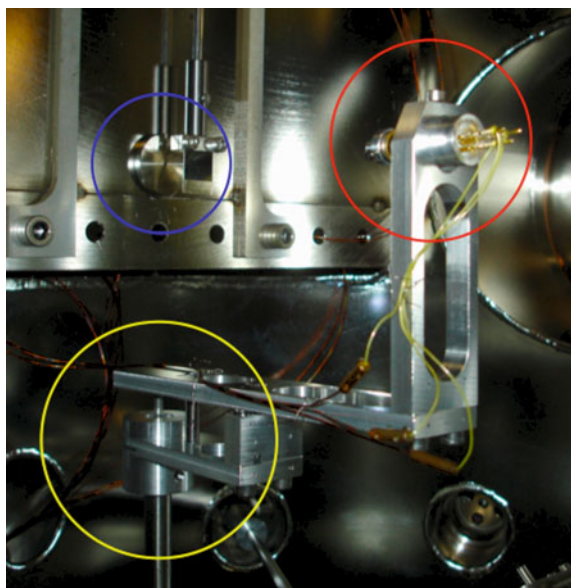
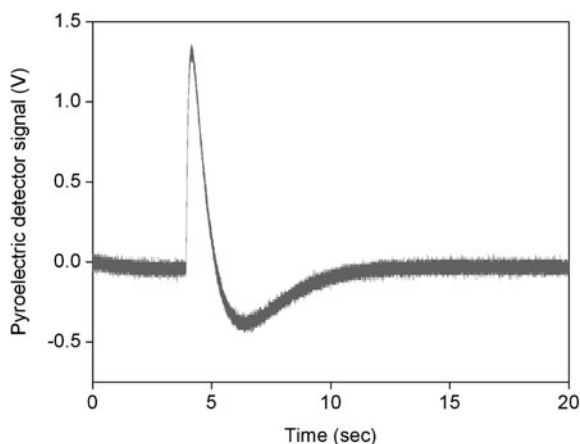


Fig. 2.25 Response of the pyroelectric detector (10x amplification) translational energy deposited by a 34 kJ/mol CW molecular beam



after introduction of the CW molecular beam, the pyroelectric detector has re-stabilized to its baseline signal of 0 V.

Figure 2.26 shows the optical setup for pyroelectric detection of IR absorption in a CW molecular beam. IR absorption of methane in a continuous molecular beam is detected by modulating the resonant excitation laser light (ON/OFF) via a shutter (Uniblitz) at a frequency within the bandwidth of the pyroelectric detector circuit (5 Hz). This modulation produces a signal proportional to the number of excited molecules prepared with by laser excitation. We lock-in detect the modulated signal from the pyroelectric detector amplified 95x via the aforementioned

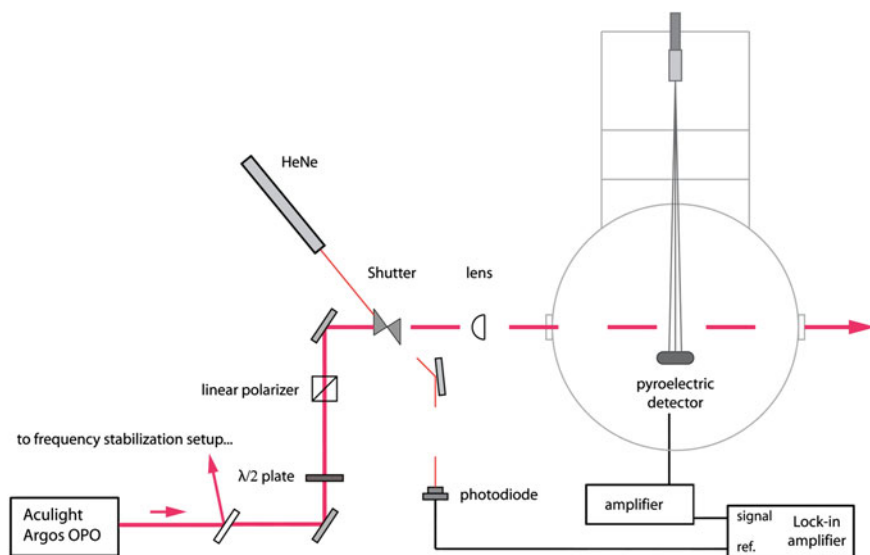
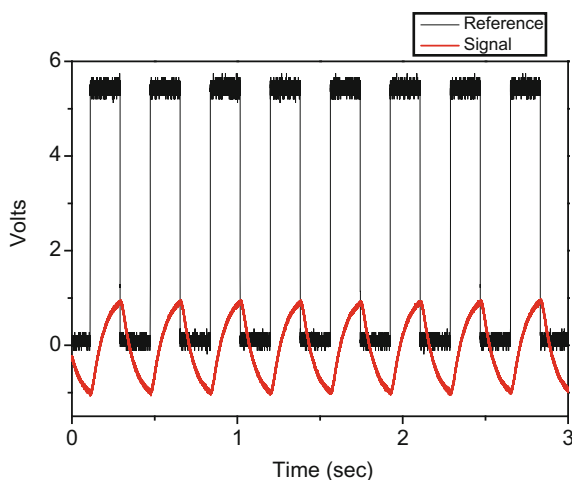


Fig. 2.26 Optical layout for pyroelectric detection of rovibrational excitation in the molecular beam

Fig. 2.27 Response of the pyroelectric detector (95x amplification) to a CW molecular beam excited by a modulated laser beam. An example of raw signals used as the lock-in amplifier's 'Reference' and 'Signal'

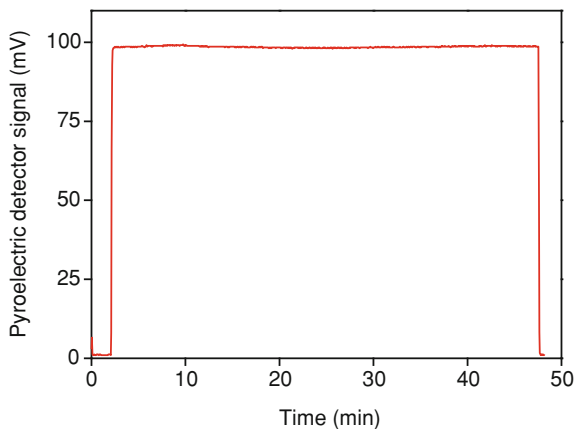


home-built amplifier. The lock-in reference is generated by a He–Ne laser passing through the open shutter.

Figure 2.27 shows the 2.75 Hz modulated signal on the pyroelectric detector (Signal trace), after 95x amplification. The reference signal (Reference trace) is used to define the frequency and phase of modulation for the lock-in amplifier.

In Fig. 2.27, the Uniblitz shutter is OPEN (laser ON) when the (Reference) photodiode is 'high' (~ 5.5 V) and the shutter is CLOSED (laser OFF) when the

Fig. 2.28 Long term stability of our frequency locking technique as observed by the lock-in detected pyroelectric signal



photodiode is 'low' (0 V). When the shutter is OPEN, the pyroelectric detector signal increases. This voltage increase corresponds to heating of the detector due to vibrational energy being deposited on the detector. When the shutter is CLOSED, the pyroelectric detector signal decreases, due to cooling of the detector. Here, the excitation is modulated at a sufficiently high rate so that the temperature of pyroelectric detector never stabilizes. This produces the saw-tooth signal shown in Fig. 2.27.

Figure 2.28 shows a trace of data collected from a lock-in detected pyroelectric detector signal using a CW molecular beam of 100% CH_4 with 3 bar backing pressure and 50 °C nozzle temperature. The excitation laser was actively stabilized to a $\text{CH}_4(\nu_3)\text{-R}(0)$ Lamb dip, as discussed in the previous section. The lock-in detected signal was 98.58 ± 0.25 mV for the 45 min measurement taken by modulating the excitation laser with a Uniblitz shutter operating at 2.75 Hz with a 50% duty cycle. Data points were collected every 3 s by reading the 'R' analog output (R, θ mode of lock-in amplifier) via 12-bit analog-to-digital conversion by a National Instruments 6023-E data acquisition card and saved in Labview. The lock-in amplifier was set to a sensitivity of 300 mV and time constant of 1 s. The signal-to-noise ratio of this measurement is ~ 400 .

Comparison of the noise of the measurement with and without the laser excitation can provide some information on the stability of the excitation setup. The standard deviation of the lock-in signal between minute 0.5 and 1.5 (no excitation) is ± 0.12 mV on a 1.06 mV signal. The standard deviation of the lock-in signal between minute 3.5 and 4.5 (modulated excitation) is ± 0.09 mV on a 98.60 mV signal. The fact that the noise is not larger with the excitation than without excitation argues that the excitation efficiency is constant on the timescale of the measurement. Furthermore, the noise in this measurement cannot be related to the frequency stability of the excitation laser since it is not due to variations in the number of excited molecules but the intrinsic noise of the measurement system. The only assertions regarding the excitation laser frequency that can be made from

this data are (1) the laser is resonant with a rovibrational transition in the molecular beam, (2) the extent of molecular beam excitation is constant on the sec timescale for nearly an hour.

In the following chapters, the method described here for pyroelectric detection of vibrationally excited molecules is used extensively to characterize the extent of excitation of the molecular beam.

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