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Progress towards a mid-infrared frequency standard using ultracold molecules

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Abstract

This thesis presents significant progress toward the development of a mid-infrared frequency standard using ultracold calcium monofluoride (CaF) molecules, as part of the QSNET project—a network of precision clocks designed to probe the temporal variation of fundamental constants. By comparing the frequency of the CaF clock with other clocks in the QSNET consortium, this work aims to measure potential variations in μ with unprecedented accuracy.

The research includes three key experiments:

- Frequency characterization of a quantum cascade laser (QCL).
- Spectroscopy of CaF’s fundamental vibrational transition.
- Development of a Raman laser system.

Further, we evaluated systematic uncertainties for the CaF lattice clock, identifying ”magic wavelengths” where ac-Stark shifts vanish. Projected uncertainties for key effects—lattice frequency, intensity, Zeeman shifts, and Doppler broadening—suggest a fractional uncertainty at the level of 10^{-17} , which is competitive as a molecular clock, and the clock will be possible to test the variation of μ .

This work bridges advanced molecular spectroscopy and precision frequency metrology, demonstrating the feasibility of a CaF-based optical lattice clock. Future efforts will focus on building and testing the CaF lattice clock, enabling new tests of fundamental physics.

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Finally, many thanks to everyone who helped me during the past a few years, I hope all of you have more happy time everyday.

I declare that this thesis is my own work. Information derived from the published and unpublished work of others has been acknowledged in the text and references are given.

All instances of 'we' in this thesis refer to collaborative work conducted jointly with CCM group members. Within these contributions, my role was primary.

Yixin Wang (2025)

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Chapter 1

Introduction-Testing the variation of fundamental constants

The great developments of atomic, molecular and optical (AMO) physics technology in recent years (e.g. laser cooling, trapping of atoms and molecules, Bose-Einstein condensation and optical frequency combs, etc.) make AMO physics a good platform for the study of physics theories and applications. For example, some AMO experiments are designed to search for new physics beyond the Standard Model with precision measurements. In this section, previous work on searching for variation of fundamental constants will be reviewed, current limit and possible future improvements will also be introduced. Theoretical and experimental study on atomic, ion and molecular clocks built for measuring the fundamental constants will be described. Finally, our proposed molecular clock will be presented.

1.1 Fundamental constants

According to the definition of [9], a fundamental constant is defined as: **Any parameter not determined by the theories in which it appears.** This definition implies that [10]:

- The number of fundamental constants depends on a particular theory.

- The fundamental constants are not predicted by any theory and thus their values must be determined through measurements.

The combination of the General Relativity (GR) and Standard Model (SM) of particle physics that combines Chromodynamics (QCD) with the electroweak theory gives one of the best model of physics nowadays. The minimal SM has 19 parameters. These fundamental constants are invariable according to their definitions in the SM. However, if some theories beyond the SM and GR are considered, the dimensionless fundamental constants can be dynamical. There are many theories related to dark matter, dark energy and unification of the fundamental forces that predict varying fundamental forces: the string theories [11], discrete quantum gravity [12], loop quantum gravity [13], chameleon models [14] and dark energy models with a nonminimal coupling of a quintessence field [15], etc.

In AMO physics, the temporal variations of fine structure constant $\alpha = e^2/(4\pi\epsilon_0\hbar c)$ and electron-to-proton mass ratio $\mu = m_e/m_p$ can be measured because the transition frequencies of atoms and molecules contain the above constants. Different transitions have different dependencies on the fundamental constants, by measuring the frequency ratios of the different transitions, the variations of fundamental constants are obtained.

1.2 Atomic and molecular clocks: theory

Atomic and molecular clocks are based on very stable transition frequencies. These transitions can be electronic, vibrational, rotational or hyperfine transitions of atoms, ions and molecules. Different transitions have different levels of frequency uncertainty and are used to measure the variations of different fundamental constants. The clock transitions usually have narrow natural linewidths and the systematic shifts are controlled to high accuracy by the modern AMO physics technologies. The SI definition of the second is based on the Cs fountain clocks [16] [17], which have an uncertainty of 10^{-16} . The state-of-the-art optical atomic clocks have achieved the fractional frequency uncertainty of 10^{-18} and below [18] [19]. Clocks based on different types

of transitions of atoms and molecules have different dependence on the fundamental constants [3]:

- **Optical clocks** Optical clocks are based on the transitions between different electronic states, and are usually in the visible frequency range. The frequency of optical transitions can be expressed as:

$$\nu_{\text{opt}} = A \cdot F_{\text{opt}}(\alpha) \cdot cR_{\infty} \quad (1.1)$$

where A is a constant that depends on the specific atomic and molecular species, F_{opt} is the relativistic correction and R_{∞} is the Rydberg constant:

$$R_{\infty} = \frac{c}{4\pi\hbar} \alpha^2 m_e \quad (1.2)$$

- **Microwave transitions** Microwave clocks are based on the transitions between hyperfine energy levels, and the frequency is written as:

$$\nu_{\text{MW}} = B \cdot \alpha^2 F_{\text{MW}}(\alpha) \cdot \mu c R_{\infty} \quad (1.3)$$

where B is a constant that depends on the specific atomic and molecular species, $F_{\text{MW}}(\alpha)$ is the relativistic correction to the microwave transition.

- **Vibrational clocks** Vibrational clocks are based on the transitions between different vibrational states of molecules. The frequency is expressed as:

$$\nu_{\text{vib}} = C \cdot \mu^{1/2} \cdot cR_{\infty} \quad (1.4)$$

where C is a constant which depends on the specific molecule and transition.

To quantify the variations of fundamental constants from the variations of atomic and molecular transitions, the sensitivity coefficient K_X is defined as:

$$K_X = \frac{\partial \ln(\nu_i / cR_{\infty})}{\partial \ln X} \quad (1.5)$$

where X denotes the fundamental constants α or μ , ν_i is the frequency of specific atomic or molecular transition.

Following the above definitions for K_X and the expressions for three types of transitions, the sensitivity coefficients K_α and K_μ for optical, microwave and vibrational transitions are expressed as:

$$K_\alpha = \begin{cases} \partial \ln F_{opt} / \partial \ln \alpha & \text{for optical transitions} \\ 2 + \partial \ln F_{MW} / \partial \ln \alpha & \text{for microwave transitions} \\ 0 & \text{for vibrational transitions} \end{cases} \quad (1.6)$$

$$K_\mu = \begin{cases} 0 & \text{for optical transitions} \\ 1 & \text{for microwave transitions} \\ 1/2 & \text{for vibrational transitions} \end{cases} \quad (1.7)$$

The way of measuring the variations of fundamental constants is to measure the frequency ratio between different clocks. The relationship of the frequency ratio between two clocks and the variation of a fundamental constant is:

$$\frac{dR}{R} = [K_{X,1} - K_{X,2}] \frac{dX}{X} \quad (1.8)$$

where $R = \nu_1/\nu_2$ is the frequency ratio between two clock transitions ν_1 and ν_2 , $K_{X,1}$ and $K_{X,2}$ are the sensitivity coefficients of the two transitions. From Eq. 1.8, transitions with a big difference in their sensitivity coefficients could make the frequency comparison measurement more sensitive to the variation of a fundamental constant. For example, frequency comparison between a vibrational clock and an optical transition can measure the variations of α and μ together.

For the measurements of the variation of α , the frequency ratio of Hg^+ and Al^+ optical clocks over the course of a year [20], yields:

$$\dot{\alpha}/\alpha = (-1.6 \pm 2.3) \times 10^{-17} \text{ yr}^{-1} \quad (1.9)$$

Another measurement is the ratio deduced from the electric quadrupole (E2) and electric octupole (E3) clock frequency measurements in Yb^+ over around 4 years [21]:

$$\dot{\alpha}/\alpha = (1.0 \pm 1.1) \times 10^{-17} \text{ yr}^{-1} \quad (1.10)$$

The present-day best constraint for μ is from the comparison of an Yb^+ optical clock with a Cs microwave clock [21]:

$$\dot{\mu}/\mu = (0.8 \pm 3.6) \times 10^{-17} \text{ yr}^{-1} \quad (1.11)$$

The constraints of α and μ have been analyzed [4] shown in Fig. 1.1. In Fig. 1.1, filled stripes mark the 1 standard deviation uncertainty regions of individual measurements and the central blank region is bounded by the standard uncertainty ellipse resulting from the combination of all data[4].

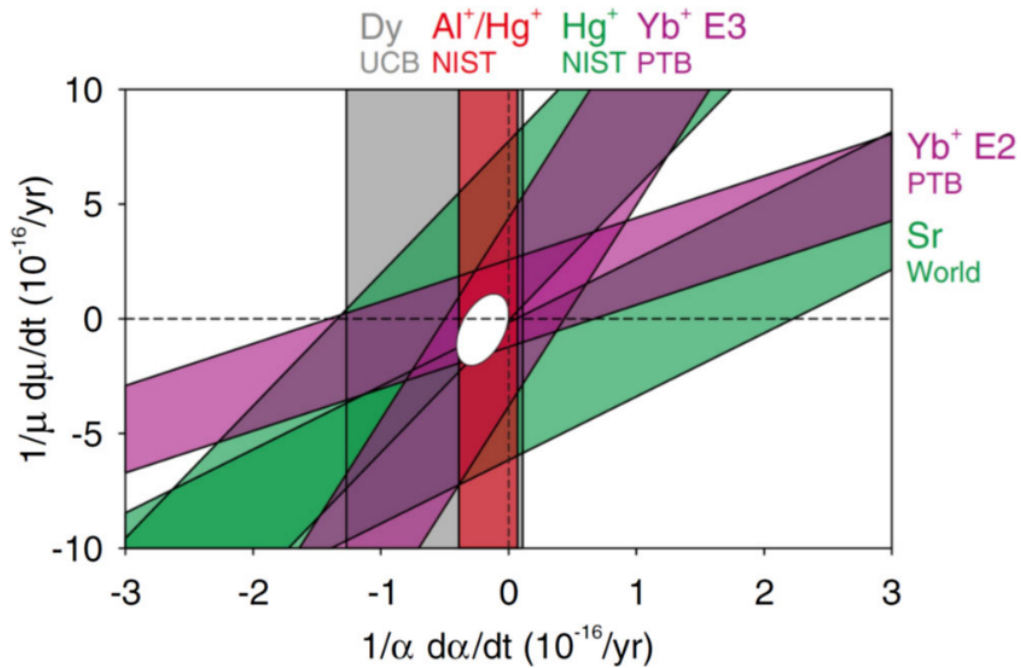


Figure 1.1: Constraints on temporal variations of α and μ from comparisons of atomic transition frequencies. From [4].

1.3 The development of clocks in experiment

The development of AMO technologies makes measuring the variations of α and μ possible. Microwave clocks were first developed to set up the frequency standard, investigated and lower frequency uncertainties. The vibrational transitions of molecules were also used for building clocks recently. These clocks will be introduced in later paragraphs. The evolution of the fractional frequency uncertainties of microwave, optical and molecular clocks shown in Fig. 1.2. This figure is adapted from [10]. The vibrational clock is from [22].

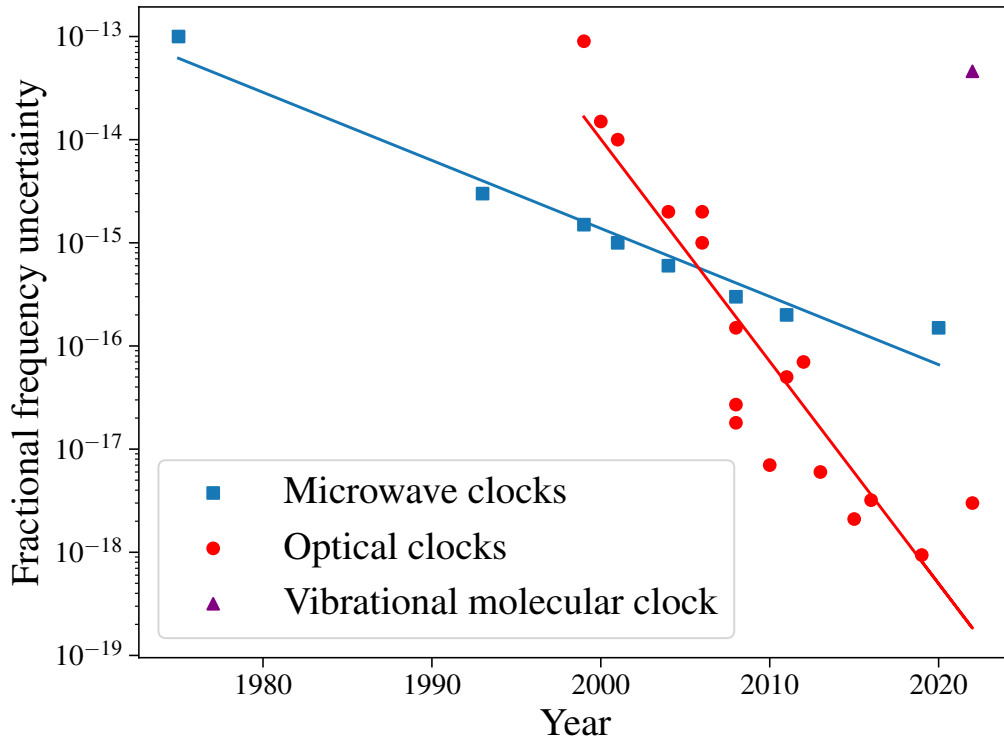


Figure 1.2: Evolution of fractional frequency uncertainties of atomic frequency standards.

The SI definition of the second is realized by the Cs fountain clocks with the uncertainty of 10^{-16} [16] [17]. This fractional uncertainty is near the practical limitations of this type of clock, because the fractional frequency uncertainty is related to the ratio $Q = f/\Delta f$ between the transition frequency f and linewidth Δf . For the microwave clocks, the quality factor Q limits the fractional uncertainty to the 10^{-16} level.

To make better frequency standards, optical clocks have been developed. For optical atomic clocks, Q can be 5 orders of magnitude higher than the microwave clocks, which means that

the optical clocks are able to reach much lower fractional uncertainties [10]. The present-day state-of-the-art atomic clocks have reached the fractional uncertainties of the 10^{-18} level. For example, the Sr lattice clock reported in [23] has a fractional uncertainty of 2×10^{-18} .

1.4 Molecular and ion clocks

Although most existing clocks are based on atomic microwave and optical transitions, clocks based on other types of transitions are also possible and can have good predictions for the variation of fundamental constants. Ions are easy to trap and they have similar transition properties to atoms, so ions are widely used for building clocks. Highly charged ions are ideal for testing the variation of α because they have very high K_α . One of the clocks with the lowest frequency uncertainty in the world is an ion clock: a $^{27}\text{Al}^+$ quantum-logic clock [18] with a systematic uncertainty of 9.4×10^{-19} is the state-of-the-art optical clock.

Due to the rich spectra with different types of transitions, molecules are suitable for testing the variations of fundamental constants, especially for μ , where pure vibrational and rotational transitions have $K_{\mu-vib} = 1/2$ and $K_{\mu-rot} = 1$. Since the extraordinary development of molecular experimental techniques like laser cooling in recent years [10], several molecular clocks have been built and the state-of-the-art uncertainty for vibrational clocks is at the 10^{-14} level [24]. A comparison in 2008 of the frequency of a rovibrational transition in SF_6 with the fundamental hyperfine transition in Cs, reported a limit on the fractional temporal variation of μ as $\dot{\mu}/\mu = (3.8 \pm 5.6) \times 10^{-14} \text{ yr}^{-1}$ [22]. More recently in 2019, a transition between a nearly degenerate pair of vibrational levels of KRb molecules is used to improve the measurement on the stability of μ , yielding $\dot{\mu}/\mu = (0.3 \pm 1.0) \times 10^{-14} \text{ yr}^{-1}$ [25]. Most recently in 2023, a molecular clock was reported based on the vibrational transition between the weakest bound and most tightly bound irrotational states $(v = 62, J = 0) \rightarrow (v = 0, J = 0)$ in the $X^1\Sigma_g^+$ ground potential of $^{88}\text{Sr}_2$ [24]. This clock reaches a systematic uncertainty of $\dot{\mu}/\mu = 4.6 \times 10^{-14} \text{ yr}^{-1}$, which is an important experimental result of the frequency standards in the THz region.

1.5 The QSNET project

All of the work included in this thesis is related to the QSNET project: 'A network of clocks for measuring the stability of fundamental constants' [3]. This project is a collaboration between theoretical and experimental physicists from different research communities in the UK. In the QSNET consortium, a series of state-of-the-art clocks and next-generation clocks are included, as illustrated in Fig. 1.3. There are seven clocks included in the consortium: the existing Sr, Yb⁺ and Cs atomic clocks at the National Physical Laboratory (NPL), a N₂⁺ molecular ion clock being built at the University of Sussex, a CaF molecular lattice clock being built at Imperial College London, and a Cf highly charged ion clock being built at the University of Birmingham. This clock network will eventually be linked with other clocks across the world. In Fig. 1.3, the nodes indicate the clocks and what they measure. The sensitivity coefficients of each clock are also shown in the right column. The definition of K_α and K_μ is given in Sec. 1.2. This figure is from [3].

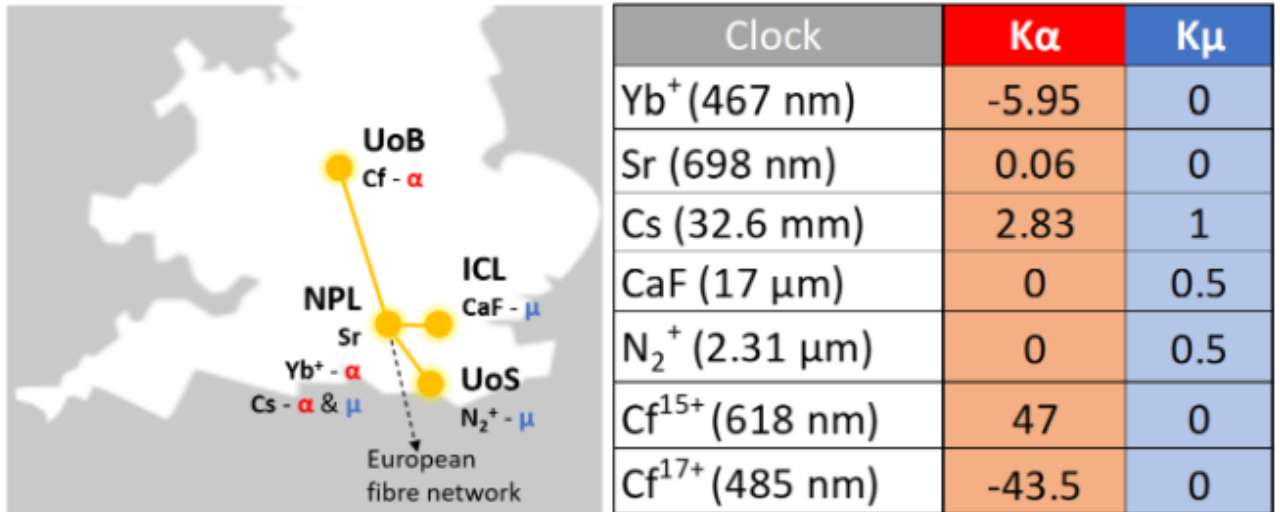


Figure 1.3: The QSNET network which includes seven clocks from different research communities.

1.6 The plan for making the CaF clock

In the QSNET consortium, the CCM group from Imperial Collge London proposed a molecular optical lattice clock based on the fundamental vibrational transition with a natural linewidth of 0.7 Hz ($v = 0 \rightarrow v' = 1$) on the- ground electronic state of CaF molecule. CaF is a diatomic molecule which is very suitable for laser cooling and making the clock. The Franck-Condon factors of CaF are very diagonal, which means the loss from the states used for cooling to other states during the cooling cycle is quite low. The vibrational transition is chosen for the clock because it is sensitive to μ . This transition has the sensitivity coefficient $K_\mu = 1/2$. The lasers and energy levels of CaF used for building the clock are shown in Fig. 1.4. In this figure, the yellow and green arrows are lasers used for laser cooling and detection. The vibrational transition in grey is the clock transition. The two red arrows are the Raman lasers used for driving the two photon ($N = 0 \rightarrow N' = 0$) transition[3].

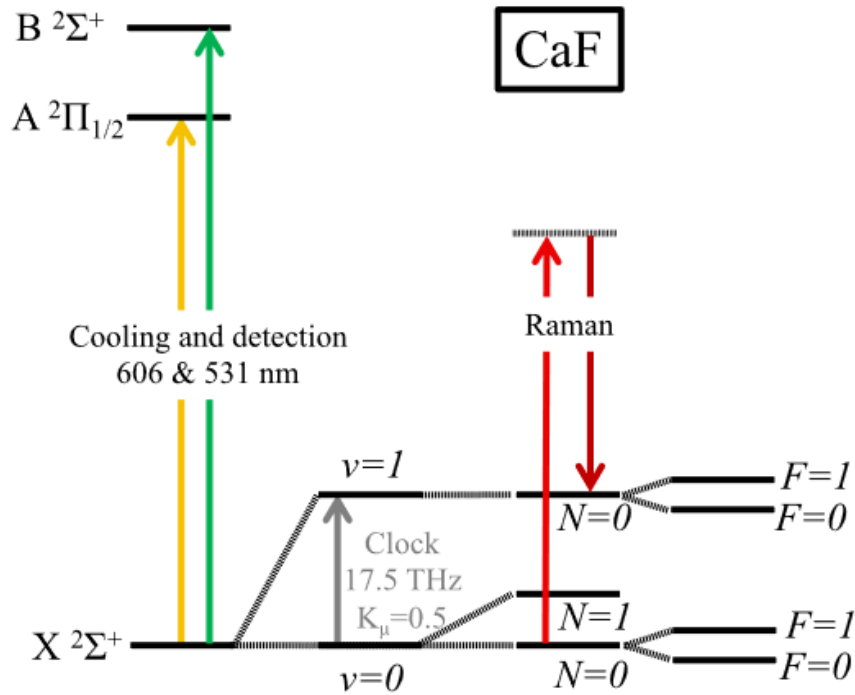


Figure 1.4: The laser and energy levels of CaF used for building the optical lattice clock. From [3].

Our plan for the clock project has several stages listed below:

1. A 17 μm Quantum Cascade Laser (QCL) has been developed [6] in order to drive the

$(v, N) = (0, 1)$ to $(v', N') = (1, 0)$ transition in the CaF ground electronic state (the grey line in Fig. 1.4). Here, v and N are the vibrational and rotational quantum numbers.

2. To calibrate this new QCL, we use several N₂O reference lines from a NIST calibration table [26] with a frequency uncertainty of 5 MHz [27]. Absorption spectroscopy of N₂O near 17 μm has been performed and the N₂O lines which have frequencies close to the CaF clock transition are measured and analyzed. This work is described in Chapter. 2.2.1.
3. An experiment for verifying the frequency of the CaF clock transition is needed because it has never been measured experimentally before. The dipole allowed $(v, N) = (0, 1)$ to $(v', N') = (1, 0)$ transition is driven using a sample of laser cooled CaF molecules with the 17 μm laser. The measurement of the frequency and its uncertainty of this CaF vibrational transition is based on N₂O spectroscopy mentioned in the previous step. The frequency uncertainty can be measured to ≈ 10 MHz, which is a good first prediction for the clock transition. This part will be described in Chapter. 4.
4. A Raman system to drive the $(v, N) = (0, 0)$ to $(v', N') = (1, 0)$ clock transition of CaF is being built. Two Raman lasers (1064 nm and 1134 nm) are locked to an ultra-stable cavity using the Pound-Drever-Hall technique. The CaF molecules will be cooled and trapped in an optical lattice. The clock transition will be driven in the lattice using the Raman lasers and the frequency uncertainty will be estimated. The plan for this experiment is described in Chapter. 5.

Chapter 2

Molecular spectroscopy of CaF and N₂O: theory

In this chapter, some theoretical background of molecular spectroscopy is introduced. The quantum numbers, selection rules for transitions, the parities and Hund's cases are reviewed in this chapter. Some basic information about the molecules (N₂O, CaF) used in our experiment is also provided.

2.1 Molecular spectroscopy

For molecules, there are relative motions between different atoms which form the molecule. Many energy levels will appear from these motions. Within the Born-Oppenheimer approximation the wave functions of atomic nuclei and electrons in a molecule can be treated separately, based on the fact that the nuclei are much heavier than the electrons. The molecular wavefunction is written as:

$$\phi_{n,\nu,J,M}(R, r_i) = \phi_n(R; r_i) R^{-1} f_\nu(R) Y_{JM}(\Theta, \Phi) \quad (2.1)$$

where $\phi_n(R; r_i)$ is the electronic part, $R^{-1}f_v(R)$ is the vibrational part and $Y_{JM}(\Theta, \Phi)$ is the rotational part, where r_i are the displacements of the electrons, while (R, Θ, Φ) are the spherical polar coordinates of one nucleus relative to the other. The index n labels the electronic state, v labels the vibrational state, J is the rotational angular momentum quantum number, and M is the projection of the rotational angular momentum onto the z -axis. They will be introduced separately in the sections below.

2.1.1 Rotational spectroscopy

According to the moments of inertia, molecules can be classified into five types: linear molecules (e.g. CaF and N₂O), spherical tops, prolate symmetric tops, oblate symmetric tops and asymmetric tops. Different types of molecules are described by different sets of quantum numbers for rotational and vibrational levels. The molecules used in our experiment, CaF and N₂O are both linear molecules, so only this type is introduced here.

The classical expression for the rotational kinetic energy of a rigid linear molecule is:

$$E_k = \frac{1}{2}R_x\omega_x^2 + \frac{1}{2}R_y\omega_y^2 + \frac{1}{2}R_z\omega_z^2 = \frac{R_x^2}{2I} + \frac{R_y^2}{2I} = \frac{R^2}{2I} \quad (2.2)$$

where I_x, I_y, I_z are moments of inertia of molecules, $\omega_x, \omega_y, \omega_z$ are angular velocities. For linear molecules, $I_z = 0, I_x = I_y = I$, R is the rotational angular momentum. Then the rotational Hamiltonian is:

$$\hat{H} = \frac{\hat{R}^2}{2I} \quad (2.3)$$

After solving the Schrodinger equation, the rotational energy $F(R)$ is:

$$F(R) = BR(R+1) \quad (2.4)$$

where B is the first order rotational spectroscopic constant. Considering the centrifugal distortion when a molecule rotates, the centrifugal distortion constant D and additional higher order

distortion correction constants are introduced:

$$F(R) = BR(R+1) - D[R(R+1)]^2 + H[R(R+1)]^3 + L[R(R+1)]^4 + \dots \quad (2.5)$$

The transition dipole moment of a pure rotational transition is:

$$\mathbf{M} = \int \varphi_{J'M'} \boldsymbol{\mu} \varphi_{JM} d\tau \quad (2.6)$$

where $\varphi_{J'M'}$ and φ_{JM} are wavefunctions of the upper and lower states in a transition, $\boldsymbol{\mu}$ is the transition dipole moment.

The wavefunction for a linear molecule is written as:

$$\varphi_{JM} = Y_{JM}(\Theta, \Phi) \quad (2.7)$$

where Θ and Φ are angles associated with the spherical harmonics Y_{JM} .

Using equations Eq. 2.6 and Eq. 2.7, we can find the selection rules for rotational transitions:

$$\Delta M = 0, \pm 1 \text{ and } \Delta J = \pm 1.$$

2.1.2 Vibrational spectroscopy

The Schrodinger equation for describing the vibration in a diatomic molecule is:

$$\frac{-\hbar^2}{2\mu} \nabla^2 \phi + V(r) \phi = E \phi \quad (2.8)$$

Many empirical forms have been developed for $V(r)$. One common approach is to use a Taylor series expansion about the equilibrium internuclear separation r_e :

$$V(r) = V(r_e) + \left. \frac{dV}{dr} \right|_{r_e} (r - r_e) + \frac{1}{2} \left. \frac{d^2V}{dr^2} \right|_{r_e} (r - r_e)^2 + \dots \quad (2.9)$$

where $\frac{dV}{dr}|_{r_e} = 0$. The corresponding eigenvalues for a harmonic oscillator are:

$$E_v = \hbar \frac{d^2V}{dr^2}(v + 1/2) = \hbar\omega(v + 1/2), \quad v = 0, 1, 2 \quad (2.10)$$

This model is a good approximation for low vibrational states in a molecule.

The Morse potential is another model for $V(r)$. It asymptotically approaches a dissociation limit $V(r) = D$ as $r \rightarrow \infty$:

$$V(r) = D(1 - e^{-\beta(r-r_e)})^2 \quad (2.11)$$

The eigenvalues for the Morse potential can be written as:

$$E = \hbar\omega_e(v + \frac{1}{2}) - \hbar\omega_e\chi_e(v + \frac{1}{2})^2 + B_e[J(J+1)] - D_e[J(J+1)]^2 - \alpha_e(v + \frac{1}{2})[J(J+1)] \quad (2.12)$$

The transition dipole moment for a vibrational transition is written as:

$$\mathbf{M}_{v'v''} = \int f_v' \boldsymbol{\mu}(r) f_v'' dr \quad (2.13)$$

Expand $\boldsymbol{\mu}(r)$ into Taylor series about $r = r_e$:

$$\boldsymbol{\mu} = \boldsymbol{\mu}_e + \frac{d\boldsymbol{\mu}}{dr}|_e(r - r_e) + \frac{1}{2} \frac{d^2\boldsymbol{\mu}}{dr^2}|_e(r - r_e)^2 + \dots \quad (2.14)$$

then

$$\mathbf{M}_{v'v''} = \boldsymbol{\mu}_e \int \varphi_{vib}'^* \varphi_{vib}'' dr + \frac{d\boldsymbol{\mu}}{dr}|_e \int \varphi_{vib}'^* (r - r_e) \varphi_{vib}'' dr + \dots \quad (2.15)$$

The first term on the right hand side of Eq. 2.15 equals zero because wavefunctions for different vibrational states are orthogonal. The selection rule is then dominated by the second term. If the harmonic oscillator model is used, the selection rule is calculated to be $\Delta v = \pm 1$. If anharmonic model is considered, $\Delta v = \pm 2, 3, \dots$ is also allowed.

There are more cases for polyatomic molecules, the levels of linear triatomic molecules are mentioned in Sec. 2.2.

2.1.3 Electronic spectroscopy

For diatomic molecules, the electronic Schrodinger equation is:

$$\hat{H}_{el}\phi_n = E_{el}\phi_n \quad (2.16)$$

where the Hamiltonian has the similar expression as the expression for atoms:

$$\hat{H}_{el} = \frac{-\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_i \frac{Z_A e^2}{4\pi\epsilon_0 r_{Ai}} - \sum_i \frac{Z_B e^2}{4\pi\epsilon_0 r_{Bi}} + \frac{Z_A Z_B e^2}{4\pi\epsilon_0 r_{AB}} + \sum_i \sum_{j>i} \frac{e^2}{4\pi\epsilon_0 r_{ij}} \quad (2.17)$$

where Z_A and Z_B are the atomic numbers of two atoms in a diatomic molecule, r_{Ai} and r_{Bi} are the distance between the two nuclei and electrons, r_{AB} is the distance between two nuclei and r_{ij} is the distance between electrons.

The total angular momentum $\mathbf{J}$, is the vector sum of the orbital($\mathbf{L}$), spin($\mathbf{S}$) and rotational($\mathbf{R}$) angular momenta:

$$\mathbf{J} = \mathbf{L} + \mathbf{S} + \mathbf{R} \quad (2.18)$$

The projections of the angular momenta onto the internuclear axis, and their relationship is shown in Fig. 2.1 for CaF. Λ is the projection of $\mathbf{L}$, Σ is the projection of $\mathbf{S}$ and Ω is the projection of $\mathbf{J}$. The notion for the electronic states is $^{2S+1}\Lambda_\Omega$, where Λ is marked by capital Greek letters (e.g., Σ , Π , Δ ...).

The selection rules for electronic states are:

- $\Delta\Lambda = 0, \pm 1$
- $\Delta S = 0$
- $\Delta\Sigma = 0$
- $\Delta\Omega = 0, \pm 1$

where the parities and Hund's cases are introduced in later sections.

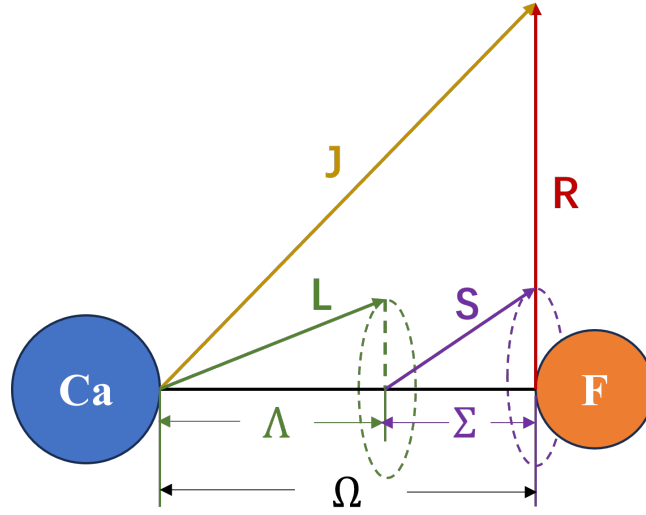


Figure 2.1: Angular momenta of CaF

2.1.4 Parities

There are several different types of parity used for molecular spectroscopy. Here is a brief introduction to them [28]:

- **Total Parity** (+/-) The symmetry operator $\hat{E}^*$ inverts all of the coordinates of the particles in the laboratory frame with the origin at the center of mass.

$$\hat{E}^* \varphi(X_i, Y_i, Z_i) = \varphi(-X_i, -Y_i, -Z_i) = \pm \varphi(X_i, Y_i, Z_i) \quad (2.19)$$

The vibrational wavefunction is unchanged by the operation because inversion of the coordinates does not change the internuclear separation r : $\hat{E}^* \varphi_{vib}(r) = \varphi_{vib}(r)$.

For the rotational wavefunctions, $\hat{E}^* |\Omega JM\rangle = (-1)^{J-\Omega} |-\Omega JM\rangle$.

For the electronic part, $\hat{E}^* |S\Sigma\rangle = (-1)^{S-\Sigma} |S, -\Sigma\rangle$.

- **Rotationless parity** (e/f) By taking J out of the total symmetry, e and f parity is defined as:

$$e : \hat{E}^* \varphi = +(-1)^J \varphi \quad (2.20)$$

$$f : \hat{E}^* \varphi = -(-1)^J \varphi \quad (2.21)$$

when J is an integer.

$$e : \hat{E}^* \varphi = +(-1)^{J-1/2} \varphi \quad (2.22)$$

$$f : \hat{E}^* \varphi = -(-1)^{J-1/2} \varphi \quad (2.23)$$

for half-integer J .

- **Gerade/Ungerade parity (g/u) and symmetric/antisymmetric (s/a) parity** These two types of parities only exist in homonuclear diatomic molecules. The g/u parity comes from the inversion operation in the point group $D_{\infty h}$, it is only applied on the electronic orbital angular momentum:

$$\hat{i} |\Lambda\rangle = \pm |\Lambda\rangle \quad (2.24)$$

The s/a parity comes from the interchange of the two identical nuclei:

$$\hat{P}_{12}(\varphi\varphi_{nuc}) = +(\varphi\varphi_{nuc}) \text{ for } I = 1/2, 2/3, 2/5... \quad (2.25)$$

$$\hat{P}_{12}(\varphi\varphi_{nuc}) = -(\varphi\varphi_{nuc}) \text{ for } I = 1, 2, 3... \quad (2.26)$$

2.1.5 Hund's cases

Hund's cases are ideal models for describing different energy level structures in rovibrational molecular spectroscopy. The strengths of the electrostatic coupling of $\mathbf{L}$ to the internuclear axis, the spin-orbit ($\mathbf{L-S}$) coupling and the coupling of $\mathbf{L}$ and $\mathbf{S}$ to $\mathbf{J}$ determine the cases for describing the specific situation. The Hamiltonian for describing a state has several components: electronic, vibrational, rotational and spin-orbit coupling operators:

$$\hat{H} = \hat{H}_{el} + \hat{H}_{vib} + \hat{H}_{rot} + \hat{H}_{so} \quad (2.27)$$

where the rotational and spin-orbit operators can be written as:

$$\hat{H}_{rot} = B(\mathbf{R})^2 = B(\mathbf{J} - \mathbf{L} - \mathbf{S})^2 \quad (2.28)$$

$$\hat{H}_{so} = A\mathbf{L} \cdot \mathbf{S} \quad (2.29)$$

Case (a) and case (b) are used to describe the experimental system of our CaF clock. The difference between case (a) and case (b) is the relative strength of spin-orbit coupling and rotational coupling.

- **case (a)** When spin-orbit coupling is large ($A \gg BJ$), the case (a) basis is the most appropriate. The good quantum numbers are Λ, S, Σ, J and Ω for case (a). The eigenvalue equations are:

$$L_\lambda |\Lambda\rangle = \Lambda |\Lambda\rangle \quad (2.30)$$

$$\mathbf{S}^2 |S, \Sigma\rangle = S(S+1) |S, \Sigma\rangle \quad (2.31)$$

$$S_\lambda |S, \Sigma\rangle = \Sigma |S, \Sigma\rangle \quad (2.32)$$

$$\mathbf{J}^2 |J, \Omega\rangle = J(J+1) |J, \Omega\rangle \quad (2.33)$$

$$J_\lambda |J, \Omega\rangle = \Omega |J, \Omega\rangle \quad (2.34)$$

where λ is the label for the internuclear axis.

- **case (b)** When spin-orbit coupling is weak enough, or is zero, ($A \ll BJ$), the states are best described in the case (b) basis. The good quantum numbers are Λ, N, S and J for case (b). The eigenvalue functions are:

$$L_\lambda |\Lambda\rangle = \Lambda |\Lambda\rangle \quad (2.35)$$

$$\mathbf{S}^2 |(N, S)J\rangle = S(S+1) |(N, S)J\rangle \quad (2.36)$$

$$\mathbf{N}^2 |(N, S)J\rangle = N(N+1) |(N, S)J\rangle \quad (2.37)$$

$$\mathbf{J}^2 |(N, S)J\rangle = J(J+1) |(N, S)J\rangle \quad (2.38)$$

$$(2.39)$$

where $\mathbf{N} = \mathbf{L} + \mathbf{R}$.

Hund's cases (c), (d) and (e) describe the cases when the separation between electronic states can be smaller than spin-orbit coupling and rotational coupling:

- **case (c)** where the spin-orbit coupling is much larger than the separation between electronic states and the rotational coupling: $A \gg BJ$ and $A \gg \Delta E_{states}$.
- **case (d)** where the rotational coupling is much stronger than the separation between electronic states.
- **case (e)** this case can describe the Rydberg states converging to ionic states with spin-orbit coupling (e.g. $^2\Pi$).

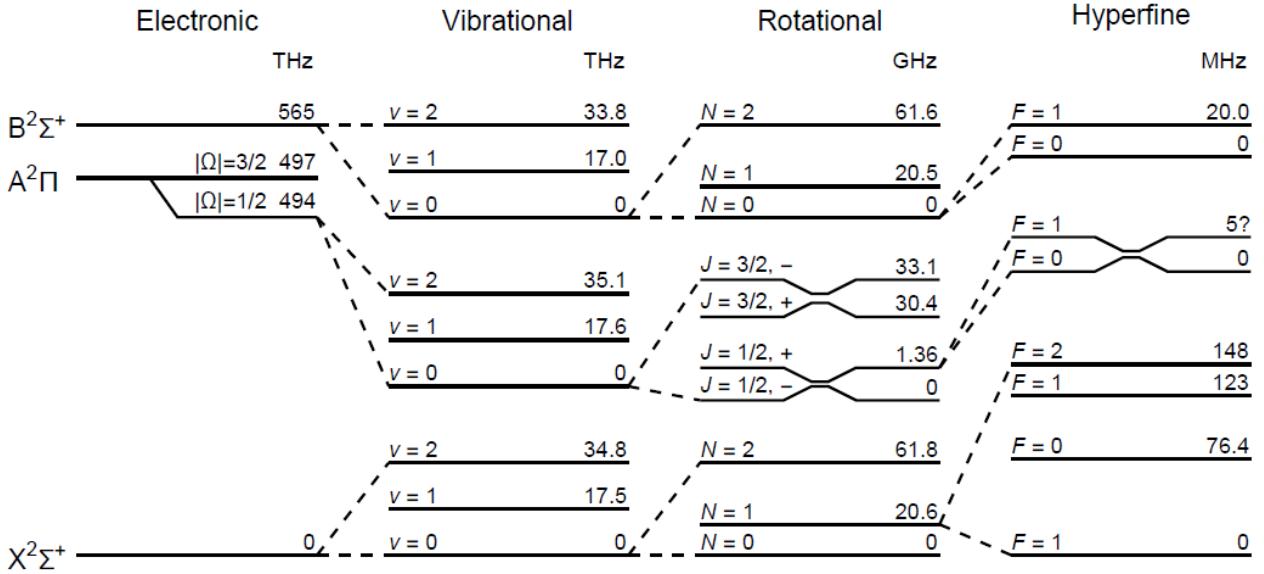
For our experiments with CaF, only Hund's cases (a) and (b) are used. Further information will be presented in later chapters.

2.1.6 CaF

CaF is a diatomic molecule, labelled using the quantum numbers presented in Tab. 2.1. In our experiment, the electronic states $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ are used for laser cooling. The target transition for making the molecular clock is the $(v', N', v, N) = (1, 0, 0, 0)$ transition, which will be driven by a Raman laser system. We also use a $17\ \mu\text{m}$ laser to drive the electric-dipole allowed $(v', N', v, N) = (1, 0, 0, 1)$ transition. This experiment is used for verifying the frequency of the CaF clock transition. When the clock is built and CaF transitions, the frequency information from CaF will also be used to calibrate back to N_2O for a frequency standard around $17\ \mu\text{m}$. The level structure of CaF is shown in Fig. 2.2.

Table 2.1: Quantum labels used for CaF

Quantum label	Description
η	Electronic state, e.g. $X^2\Sigma^+$ for CaF
ν	Vibrational quantum number
J	Rotational quantum number (for Hund's case (a))
N	Rotational quantum number (for Hund's case (b))
e/f	Rotationless parity

Figure 2.2: CaF level structure of the $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ electronic states [5]

2.2 Linear triatomic molecules

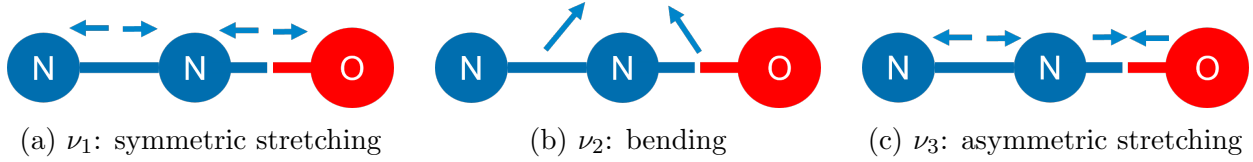
Tab. 2.2 describes the types of molecules based on the moments of inertia. The labeling scheme for the axes used in Tab. 2.2 is based on the magnitude of the moments of inertia: $I_A \leq I_B \leq I_C$, where the A -, B -, C - axes are chosen by some geometrical conventions.

Because the molecule used in our experiment, N₂O, is a linear triatomic molecule, only this case will be discussed. General knowledge for molecules, especially diatomic molecules has been provided in the previous section, here only the case for linear triatomic molecules is discussed. For linear triatomic molecules, there are three vibrational modes: symmetric stretching, bending and asymmetric stretching. These modes are shown in Fig. 2.3 using N₂O as an example.

For the bending mode ν_2 , there is an associated angular momentum l . This term must be

Table 2.2: Five types of molecules

Cases	Moments of inertia
Linear molecules	$I_B = I_C, I_A = 0$
Spherical tops	$I_A = I_B = I_C$
Prolate symmetric tops	$I_A < I_B = I_C$
Oblate symmetric tops	$I_A = I_B < I_C$
Asymmetric tops	$I_A < I_B < I_C$

Figure 2.3: Vibrational modes of N_2O .

considered in the total angular momentum $\mathbf{J}$:

$$\mathbf{J} = \mathbf{R} + \mathbf{L} + \mathbf{S} + \mathbf{l} \quad (2.40)$$

A two-dimensional harmonic oscillator can be used to model ν_2 :

$$\hat{H} = \frac{-\hbar^2}{2\mu} \left[\frac{1}{\rho} \frac{\partial}{\partial \rho} \left(\rho \frac{\partial}{\partial \rho} \right) + \frac{1}{\rho^2} \frac{\partial^2}{\partial \phi^2} \right] + \frac{1}{2} k \rho^2 \quad (2.41)$$

The wavefunction for ν_2 is written as:

$$\varphi_{\nu l} = R_{\nu l}(\rho) e^{il\phi} \quad (2.42)$$

where l is the quantum number associated with ν_2 with the angular momentum of $\pm |l| \hbar$:

$$\hat{p}_z \varphi_{\nu l} = l \hbar \varphi_{\nu l} \quad (2.43)$$

where the operator for vibrational angular momentum $\hat{p}_z$ is:

$$\hat{p}_z = i \hbar \frac{\partial}{\partial \phi} \quad (2.44)$$

From the solution of the above equations, the possible values of $|l|$ are $\nu, \nu - 2, \dots, 0$ or 1 . The selection rule for l is $\Delta l = \pm 1$.

According to the molecular wavefunction Eq. 2.1, the quantum labels used for describing the states are in Table. 2.3.

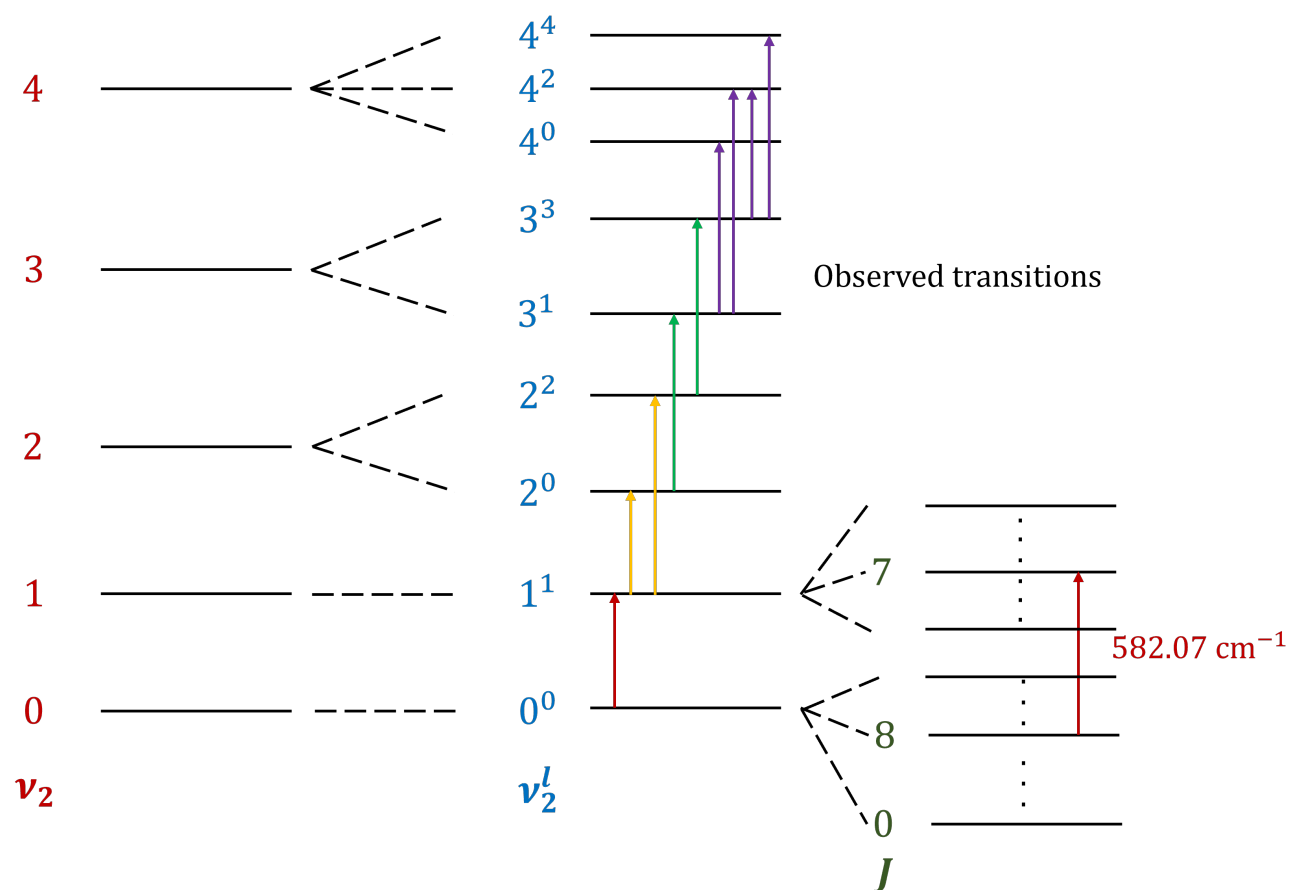
Table 2.3: Quantum labels used for N₂O

Quantum label	Description
η	Electronic state, e.g. $X^1\Sigma^+$ for N ₂ O
ν_1	Symmetric stretching vibrational mode
ν_2	Bending vibrational mode
l	Vibrational angular momentum associated with ν_2 mode
ν_3	Antisymmetric stretching vibrational mode
J	Total angular momentum
e/f	Rotationless parity

2.2.1 N₂O

N₂O is a linear triatomic molecule with the structure of $N - N - O$. Its energy levels are described by the set of quantum numbers in Table 2.3. The ground electronic state of N₂O is $X^1\Sigma^+$. Rovibrational transitions in the ground electronic state are measured in our experiment. The total quantum number J is used to describe the rotational levels, $P(J)$, $Q(J)$ and $R(J)$ are used to denote transitions with $J' = J - 1$, $J' = J$ and $J' = J + 1$, where J' and J denote the upper and lower total angular momenta.

We used a laser at $17\ \mu\text{m}$ to do absorption spectroscopy of N₂O. Rovibrational transitions in different vibrational bands on the ground electronic state are recorded in our experiment, they are presented in Fig. 2.4. In this figure, The ν_2 column is the $(\nu_1\nu_2\nu_3) = (0\nu_20)$ band, l in the second column is the angular momentum associated with the bending vibrational mode ν_2 . The J column is the total rotational angular momentum. Transitions between different vibrational bands are labeled in different colors in the ν_2^J column. The marked red transition is a well calibrated line (ν_2 P(8) line) whose frequency is very close to that of the CaF fundamental vibrational frequency. More N₂O spectra are shown in Chapter 3.

Figure 2.4: N_2O level structure.

Chapter 3

N₂O spectroscopy around 17 μm

To build the CaF vibrational clock, the frequency of the clock transition needs to be known with sufficient accuracy that the Raman transition can be found without excessive frequency scanning. A precision of a few MHz would be sufficient. Because this transition has never been driven before, the Imperial CaF clock team decided to first drive the vibrational transition directly using a custom-built laser operating at 17 μm . Then, we need a way to determine the frequency of this laser. There are no wavemeters in this spectral region. Fortunately, N₂O has many spectral lines in this region, and a few of these have been calibrated previously with a precision of a few MHz. So, we use N₂O absorption spectroscopy to calibrate the frequency of the 17 μm laser, and subsequently use the 17 μm laser to drive the vibrational transition in CaF. The N₂O spectroscopy was itself a major project that led to a lot of useful new data. This chapter begins with an introduction to the spectroscopy of N₂O, followed by a description of the methods used. The spectroscopic results are presented and analyzed, yielding a full list of the frequencies and amplitudes of a large set of spectral lines.

3.1 Mid-infrared spectroscopy and N₂O

The mid-infrared is an important region for spectroscopy, with applications in trace gas detection, environmental monitoring, quality control in chemical processes, frequency metrology,

and tests of fundamental physics. The wavelength region between 2 and 20 μm is known as the molecular fingerprint region, because every molecule has a unique spectrum in this region. However, the spectroscopic potential of this region has been difficult to exploit because (i) spectra are often crowded, requiring high resolution, (ii) laser technology in many parts of this region is often poorly developed or non-existent, (iii) optical elements often absorb strongly, especially beyond 15 μm , (iv) there are not many absolute frequency standards in this spectral region, and (v) calibration of the frequency axis when the wavelength $\lambda > 12 \mu\text{m}$ is difficult. A new generation of quantum cascade lasers at wavelengths beyond 10 μm is helping to solve some of these problems, see e.g. [29, 6], etc. Recent advances in cooling and controlling neutral molecules [30, 31] and molecular ions [32] raise the prospect of a set of frequency standards in the mid-infrared, based on the vibrational frequencies of trapped molecules, whose precision could match that available in the microwave and optical domains. These frequency standards can then be used to calibrate large sets of spectral lines in common gases. Suitable molecular clocks are currently being developed, motivated in part by their potential to search for varying fundamental constants [24, 3, 33, 34, 35].

Nitrous oxide, N_2O , is one common gas that is already used for frequency calibration in the mid infrared [36]. Environmental monitoring of this gas is important since it is the dominant anthropogenic cause of ozone depletion and is a potent greenhouse gas whose atmospheric concentration has been rising for decades [37]. The fundamental vibrational frequency of the bending (ν_2) mode of N_2O lies near 17 μm . The gas has a forest of strong absorption lines in this spectral region which have been studied extensively.

N_2O is a linear triatomic molecule with a $^1\Sigma$ ground state. Vibrational states are labelled as $(\nu_1 \nu_2^l \nu_3)$ where $\nu_{1,2,3}$ are the quantum numbers of the symmetric stretch mode, the bending mode and the antisymmetric stretch mode respectively, and l is the angular momentum associated with the bending mode. The rotationless parity e and f are used to denote l -type doubling states. Rotational transitions that have $J' = J - 1$, $J' = J$ and $J' = J + 1$ are denoted as $P(J)$, $Q(J)$ and $R(J)$ respectively, where J and J' are the rotational angular momentum quantum numbers of the lower and upper levels.

Spectroscopic data for N_2O around $17\ \mu m$ have been presented by Maki et al. [26]. The linelist from Maki et al. [26] makes use of high-precision data from heterodyne frequency measurements [26, 38]. The uncertainties of the frequency measurements of the ν_2 band reaches 3 MHz, but the frequency data for this band are not measured directly. Instead, they are calculated from other measured bands. Toth [39] also provides a N_2O linelist which covers a wide range of frequency using Fourier-transform spectroscopy with uncertainties range from 10 MHz to 1 GHz level. This linelist is the source of N_2O data in the HITRAN [7] database.

There has been very little prior laser spectroscopy of the ν_2 band of N_2O . In earlier work [40, 41, 42] using a lead salt laser, a set of ν_2 lines were measured with a relative precision of 30 MHz. Recently, a quantum cascade laser (QCL) operating at $17.2\ \mu m$ was developed in Paris and its spectral properties were measured using absorption lines of N_2O [43]. Wavelength modulation spectroscopy of N_2O using this QCL is demonstrated in this work, 165 lines in the small region between 580.3 and $582.5\ cm^{-1}$ are measured and their frequencies are determined. Because the method has high sensitivity and high dynamic range, lines from five different isotopologues and 12 different vibrational bands are observed (labelled by the formula $(\nu'_1\nu'_2\nu'_3) - (\nu_1\nu_2\nu_3)$): $(01^10) - (00^00)$, $(02^00) - (01^10)$, $(02^20) - (01^10)$, $(03^10) - (02^00)$, $(03^10) - (02^20)$, $(03^30) - (02^20)$, $(04^00) - (03^10)$, $(04^20) - (03^10)$, $(04^20) - (03^30)$, $(11^10) - (10^00)$, $(12^00) - (11^10)$, $(12^20) - (11^10)$. The QCL has been designed so that its frequency coincides with the fundamental vibrational frequency of CaF molecules. An experiment to measure this frequency with the same QCL is presented in the next chapter. In the future, the CaF transition frequency uncertainties will be calibrated to Hz level by the clock, its accuracy can be delivered to the N_2O lines, since the spectroscopy of N_2O and CaF can be performed together with the same $17\ \mu m$ QCL. These spectroscopic data will be used to establish a new frequency standard with improved accuracy around $17\ \mu m$.

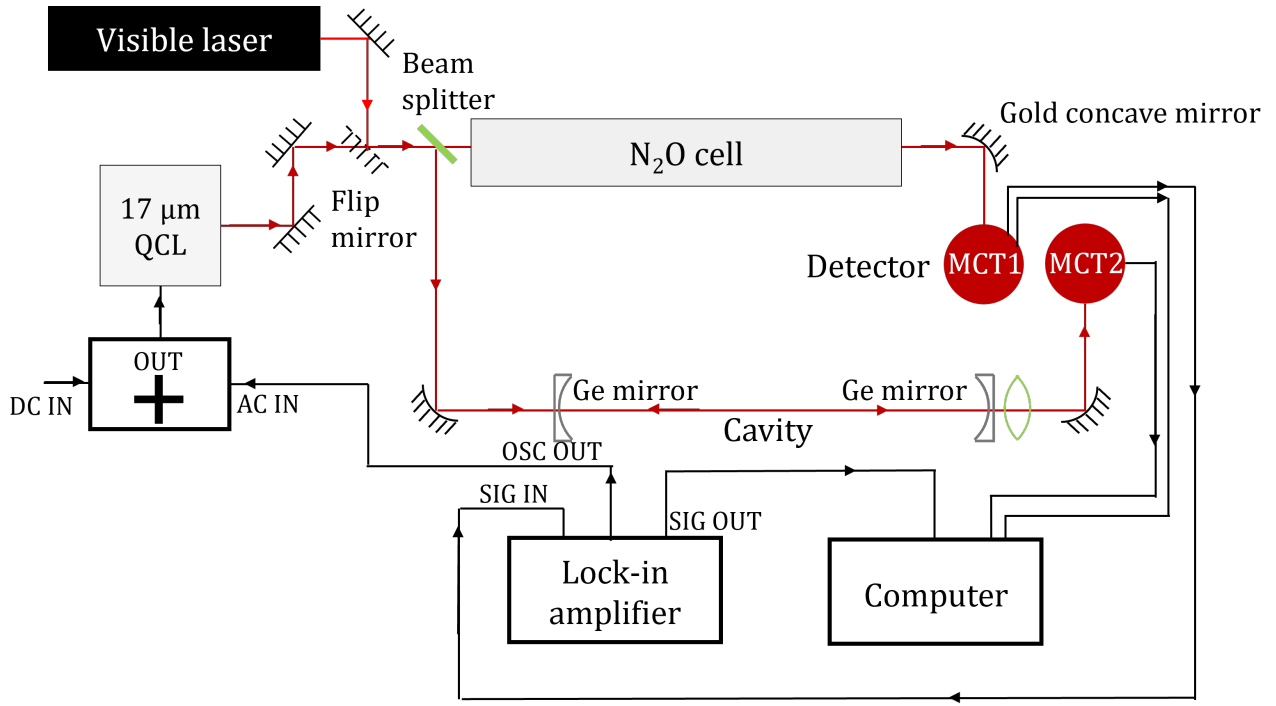


Figure 3.1: Schematic diagram of the experimental setup.

3.2 Methods

3.2.1 Experimental setup

Direct absorption spectroscopy tends to suffer from noisy signals and backgrounds that change with frequency due to the intensity changes of the laser. For these reasons, only the strongest absorption lines of N₂O could be detected this way. To improve the spectroscopy, we use a wavelength modulation technique. In this technique, the frequency of the laser is modulated and the absorption signal recorded at the modulation frequency (or a harmonic of it). In this way, only the noise at the modulation frequency enters into the measurement, and linear changes of intensity with frequency are removed. Figure 3.1 illustrates the experimental setup we use for wavelength modulation spectroscopy. The light from the QCL is separated into two beams, each with a power of approximately 0.5 mW. The first beam, used for absorption spectroscopy, passes through a cylindrical gas cell (with wedged ZnSe windows) of length 20 cm containing about 350 Pa of pure N₂O, and then onto a liquid nitrogen cooled mercury cadmium telluride detector, MCT1, that measures its power. When recording measurements without N₂O, the valve connected to the N₂O dewar will be closed, and the gas cell will be pumped to vacuum.

By applying an oscillating component to the current of the QCL, its frequency is modulated with $f_{\text{mod}} = 2.22\ \text{kHz}$ and a modulation amplitude of roughly $20\ \text{MHz}$. This modulation amplitude was chosen to give the best signal-to-noise ratio without significantly broadening the lines. However, since the modulation amplitude is comparable to the typical linewidths of about $36\ \text{MHz}$, it is necessary to include the effects of the modulation in the lineshape model, as we discuss later and in Appendix A. A lock-in amplifier detects the amplitude of the oscillating signal at MCT1 at either f_{mod} or $2f_{\text{mod}}$. The second beam, used to calibrate the frequency scale, passes through a confocal cavity and then onto a separate detector, MCT2. The cavity is formed from a pair of plano-concave lenses separated by $30\ \text{cm}$ and made from germanium whose refractive index at $17.2\ \mu m$ is $n = 3.9997$, giving a reflectivity of 35.9% . The cavity provides a set of frequency markers with a spacing of $\delta f = c/(4L) \approx 250\ \text{MHz}$. The signals from MCT1, MCT2 and the lock-in amplifier are recorded simultaneously using an oscilloscope.

3.2.2 The $17\ \mu m$ QCL

The QCL at $17\ \mu m$ from a laser company Mirsense has been characterized [6]. Using FTIR spectroscopy, the QCL can output optical power up to several milliwatts with a frequency range of $\sim 80\ \text{GHz}$. The output frequency can be tuned by the temperature and current sent to the laser diode. This laser has a frequency noise of $200\ \text{kHz}$ full width at half maximum (FWHM) for an integration time of $100\ \text{ms}$. Figure 3.2 [6], shows how the power and frequency of the QCL change with temperature and current: a) $17.3\ \mu m$ QCL output optical power and voltage versus drive current, recorded at a range of QCL temperatures. b) Spectra of the QCL, measured by a FTIR spectrometer, recorded at a range of QCL temperatures and drive currents [6].

3.2.3 Detection of the $17\ \mu m$ laser beam

Normal photodiodes with detection range in the visible and near-infrared region can not work in the $17\ \mu m$ wavelength range. Special Mercury Cadmium Telluride (MCT) detectors are used

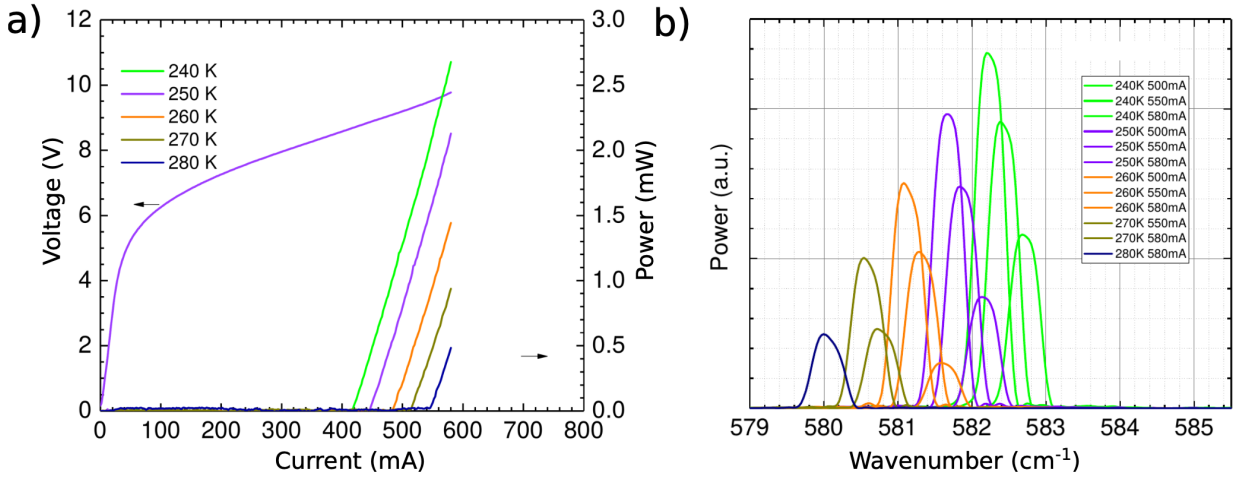


Figure 3.2: Power and frequency information of the QCL, from [6].

for detecting the laser beam power (shown in Fig. 3.3). These MCT detectors have to be cooled with liquid nitrogen and work with preamplifiers to record $17\ \mu\text{m}$ laser power of microwatts level.

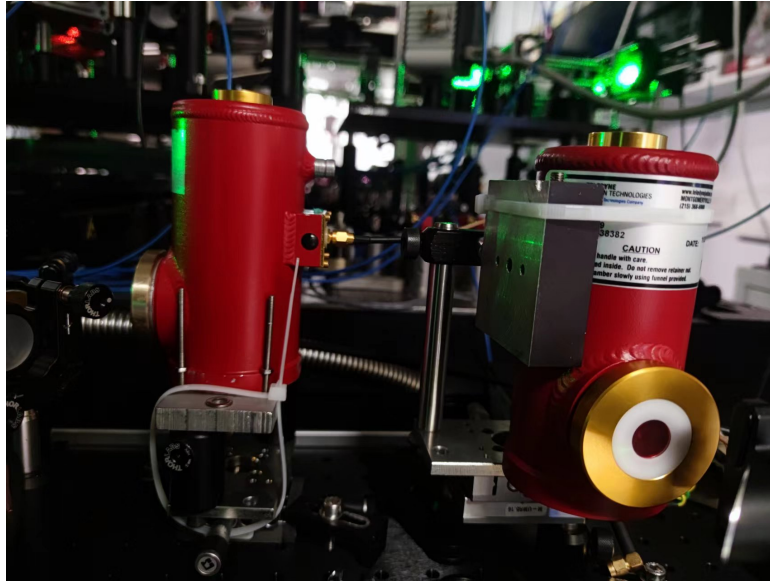


Figure 3.3: MCT detectors for $17\ \mu\text{m}$ lasers.

3.3 Wavelength modulation spectroscopy

Wavelength modulation spectroscopy is a widely used technique to detect weak transition signals that might otherwise be obscured by backgrounds or noise from the laser and detectors.

In this technique, a periodic reference signal (usually a sine wave) from a lock-in amplifier is sent to the laser, then the lock-in amplifier multiplies the signal from detector and the reference input signal. The final output from the lock-in amplifier is a low-pass filtered integration of the multiplied result over a time period. A block diagram of a lock-in amplifier is shown in Fig. 3.4.

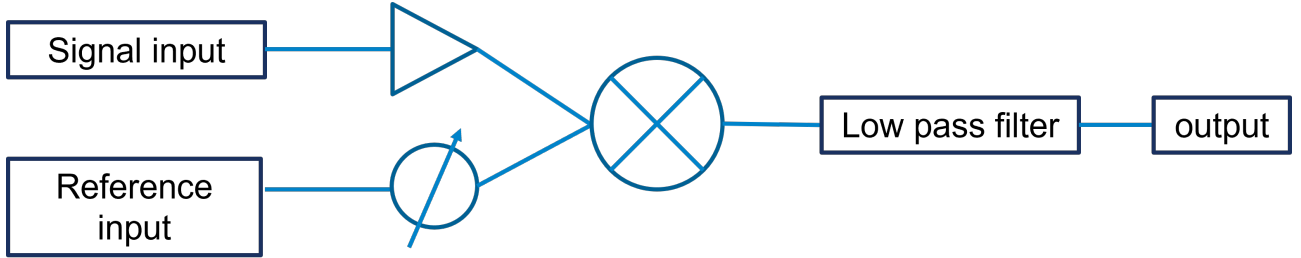


Figure 3.4: Block diagram of a lock-in amplifier.

Modulation helps significantly in measuring some weak lines, like the case in Fig. 3.5: the x axis is the output frequency of the QCL. The y axis is the signal in Volts which shows the laser power level received by the MCT detector. The upper figure shows a section of original spectrum, the background is sloping because the output power of the QCL varies with the frequency linearly. There are only 6 lines visible in this figure. The lower figure shows the same section of spectrum with $1f$ and $3f$ (nf means n th order of modulation) wavelength modulation with a modulation frequency of 2 kHz. The lineshapes are similar to 1st and 3rd derivatives of the original signal when the modulation amplitude is smaller than the transition linewidths. So the linear sloping background becomes a constant in the $1f$ data and it is gone in the $3f$ data. More lines can be observed from $1f$ and $3f$ data compared to the original data, which means the signal-to-noise ratio has been improved using wavelength modulation. However, this technique also brings distortion to the lineshape, which makes the fitting procedure more complicated (details in Appendix. A).

3.4 Results and analysis

Using wavelength modulation technique with a $17\ \mu m$ laser to perform N_2O spectroscopy, 165 lines are recorded and analyzed. We focus on a region of the spectrum centered at $581.5\ cm^{-1}$

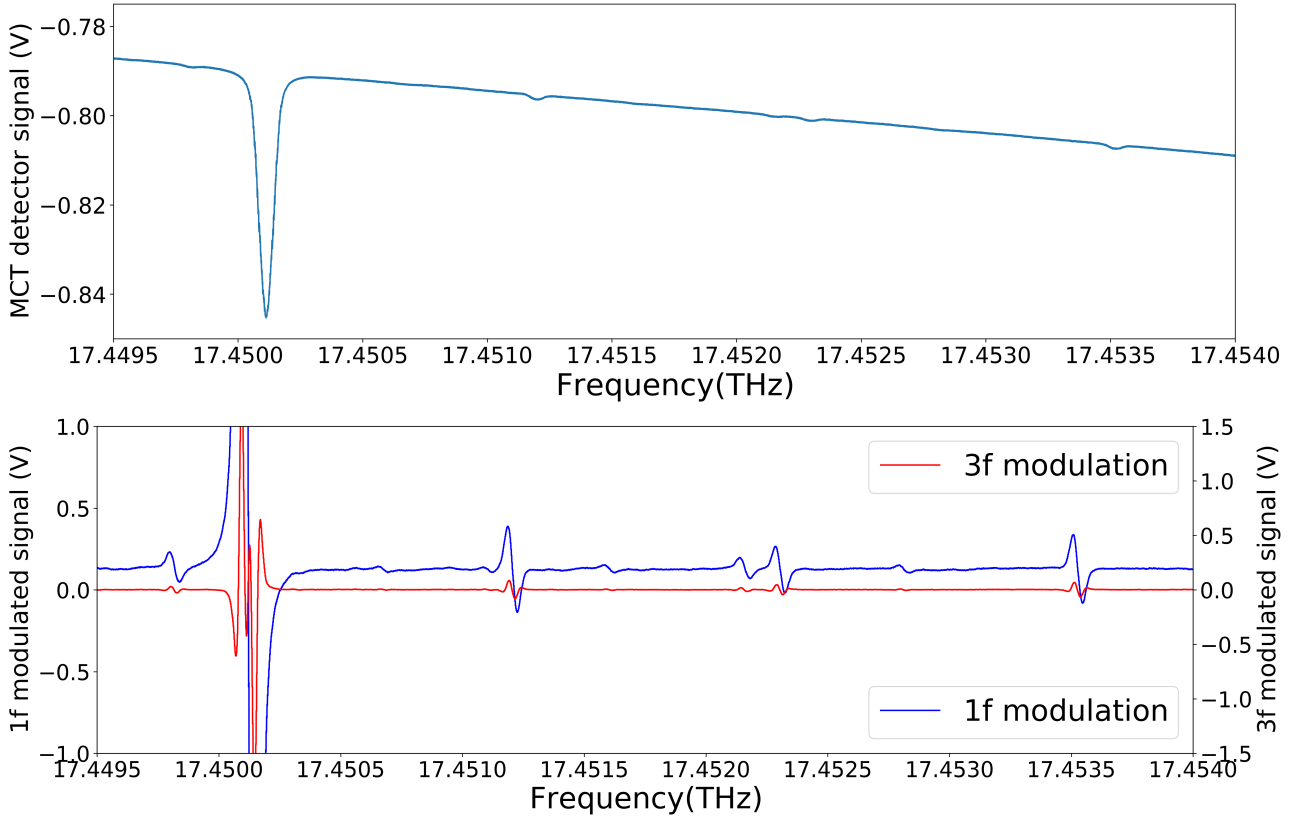


Figure 3.5: Comparison between direct absorption spectrum (upper) and demodulated spectrum (lower) in the same frequency region of N_2O .

containing strong P lines of the $(01^10) - (00^00)$ band, weaker P lines of the $(02^20) - (01^10)$ band and Q lines of the $(03^10) - (02^00)$ band, and even weaker lines from several other bands.

Figure 3.6 shows examples of the data obtained, showing the N_2O absorption signal at $2f_{\text{mod}}$ together with the cavity transmission. In the upper figure, the vertical black line indicates the position of $\text{CaF } (v', N', v, N) = (1, 0, 0, 1)$ transition. The transitions in this graph are labeled in the format of '(band)P/Q/R(J,e/f)' according to their bands: (1): $(01^10) - (000)$; (2): $(02^00) - (01^10)$; (3): $(03^10) - (02^00)$; (4): $(02^20) - (01^10)$; (5): $(04^20) - (03^10)$. The lowest figure presents the fitting to a signal detected at $2f_{\text{mod}}$, the blue dots in the lower panel are the residuals of the fitting.

3.4.1 Example data

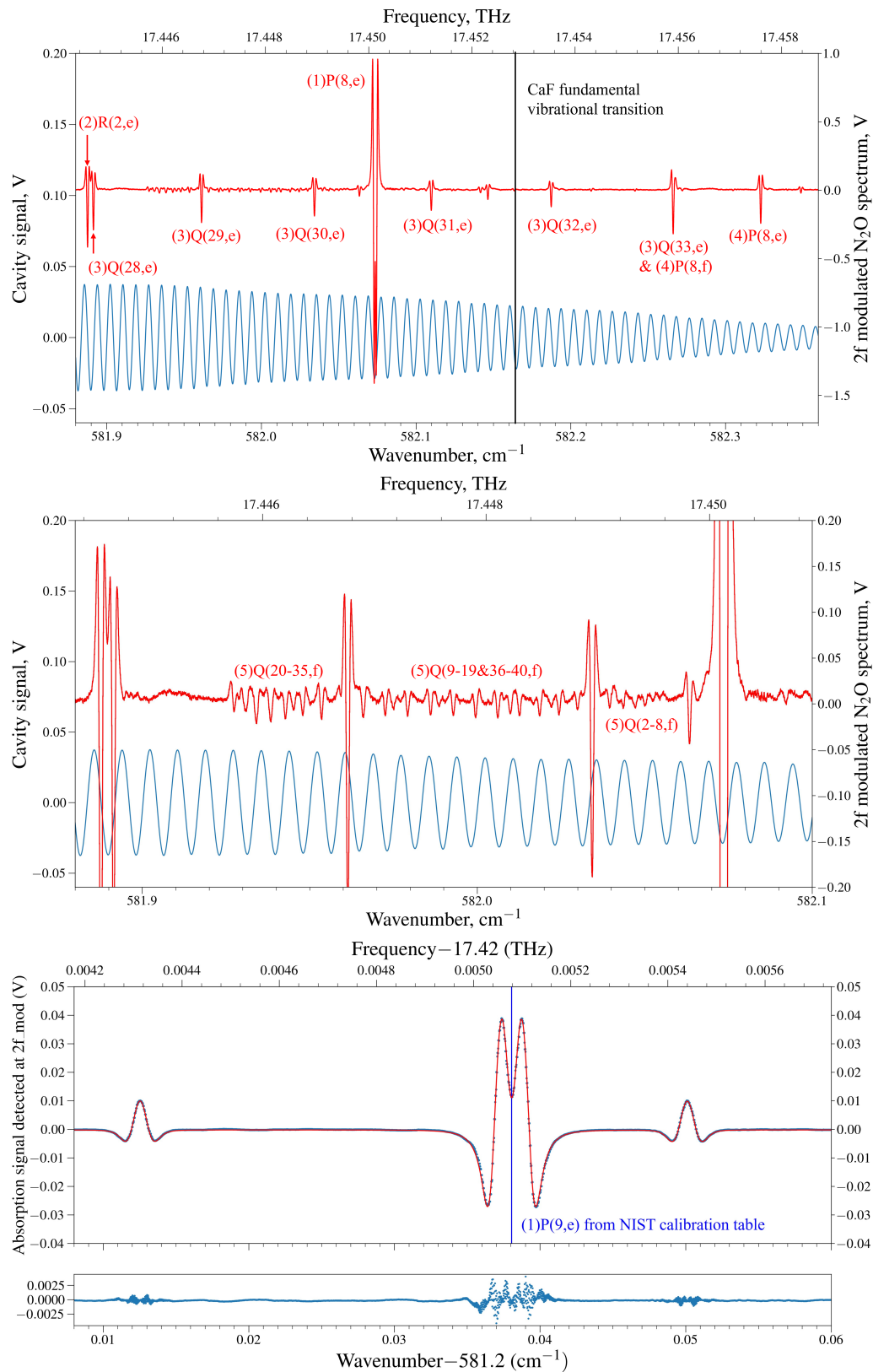


Figure 3.6: Examples of measured $^{14}N_2^{16}O$ rovibrational transitions (after detection at $2f_{mod}$, red) and cavity fringes (blue) around $17\ \mu m$.

The laser frequency is scanned at a rate of approximately 180 MHz per second and the data presented are single scans. The frequency is controlled via the QCL current which also changes the power of the laser. That change is reflected in the amplitude of the cavity fringes as the laser is scanned, and the distortion of the lineshape caused by amplitude change is considered in the fitting described in Appendix A. The DC offset of the MCT detectors is eliminated in the signal detected at $2f_{\text{mod}}$ because the scan is close to linear. The optical components are placed carefully to avoid etaloning effect from back reflections. The top figure in Fig. 3.6 shows the P(8) line in the $(01^10) - (00^00)$ band of $^{14}\text{N}_2^{16}\text{O}$, and is one of the calibration lines used in our experiment and can be found in the NIST database of calibration lines [36]. The frequencies of the calibration lines from NIST [36] are used with the cavity fringes to mark the frequencies of other lines. The other strong lines observed are mainly Q lines of the $(03^10) - (02^00)$ band in this isotopologue. The middle figure in Fig. 3.6 is an expanded view of the small region between 581.88 cm^{-1} and 582.09 cm^{-1} where we clearly observed a dense spectrum of much weaker features which are Q lines in the $(04^20) - (03^10)$ band of $^{14}\text{N}_2^{16}\text{O}$. We are in fact able to observe lines with spectral feature amplitude spanning 4 orders of magnitude.

3.4.2 Fitting to a model

Although wavelength modulation can significantly improve the SNR of the spectra, this technique also introduces distortion to the spectra. Except for the simplest Voigt profile, more modulation related parameters needs to be considered in the fitting for the spectral data. A mathematical model has been developed to describe the distorted lineshape. This model extends previous work [44, 45] and accounts for Doppler broadening, collisional broadening, the effect of the modulation, saturation of the absorption at large optical depths, and effects due to the frequency-dependence of the laser intensity. The model is important for determining accurate frequencies so we describe it in detail in the appendix and more briefly here.

The current of the QCL is modulated with angular frequency Ω , and this modulates both the frequency and intensity of the light. The detuning of the light from the centre of an absorption feature, normalized to the Voigt linewidth of the absorption feature, is denoted by Δ . It has

two parts, $\Delta = \delta - \delta_m \cos(\Omega t)$, where δ is the detuning averaged over a modulation cycle and δ_m is the modulation amplitude, both normalized to the linewidth. The laser intensity incident on the absorbing sample is $I_{in} = I_0(1 + p\Delta)$ where I_0 is at the centre of the absorption feature and we are assuming a linear dependence on Δ with proportionality constant p . We measure the intensity transmitted through the absorbing sample I_{out} and pick out the component of this signal oscillating at frequency $n\Omega$. As shown in the appendix, this component is

$$\frac{I_{out,n}}{I_0} = 2\epsilon_n(-1)^n \int_{-\delta_m}^{\delta_m} \frac{\cos\left(n \cos^{-1}\left(\frac{\delta'}{\delta_m}\right)\right)}{\sqrt{\delta_m^2 - \delta'^2}} (1 + p\delta - p\delta') e^{-\alpha(\delta - \delta')} d\delta', \quad (3.1)$$

where $\epsilon_0 = 1$ and $\epsilon_n = 2$ for all $n > 0$. The function $\alpha(\delta)$ is the optical depth and describes the frequency dependence of the absorption. In the present work, both Doppler broadening and collisional broadening are important, so we choose $\alpha(\delta)$ to be a Voigt profile,

$$\alpha(\delta) = \int_{-\infty}^{\infty} G(\delta'', \sigma_1) L(\delta - \delta'', \sigma_2) d\delta''. \quad (3.2)$$

Here $G(\delta, \sigma_1)$ is a Gaussian function with width parameter σ_1 and $L(\delta, \sigma_2)$ is a Lorentzian function with width parameter σ_2 . In cases where there are several lines close together, we choose $\alpha(\delta)$ to be a sum of Voigt profiles.

The bottom figure in Fig. 3.6 shows a small region of the spectrum around $581.2\ \text{cm}^{-1}$. The points are the measured data, and the line is a fit to the model described by Eqs. (3.1) and (3.2). The model represents the data very well, and we find that this is the case for all lines in our N_2O dataset. The free parameters in the fit are the line centre, the peak optical depth and the Gaussian and Lorentzian widths. The parameters p and δ_m are determined independently and are fixed in the fit, and we set $n = 2$ since these data are the signals at twice the modulation frequency. For the three lines in the bottom figure in Fig. 3.6: the two smaller ones have low optical depth and their profiles are similar to the second derivative of the Voigt profile. The larger one has high optical depth resulting in saturation of the absorption. This broadens the profile and introduces an extra dip at the centre of the profile which corresponds to the flat top of the saturated absorption line where the second derivative tends towards zero. This

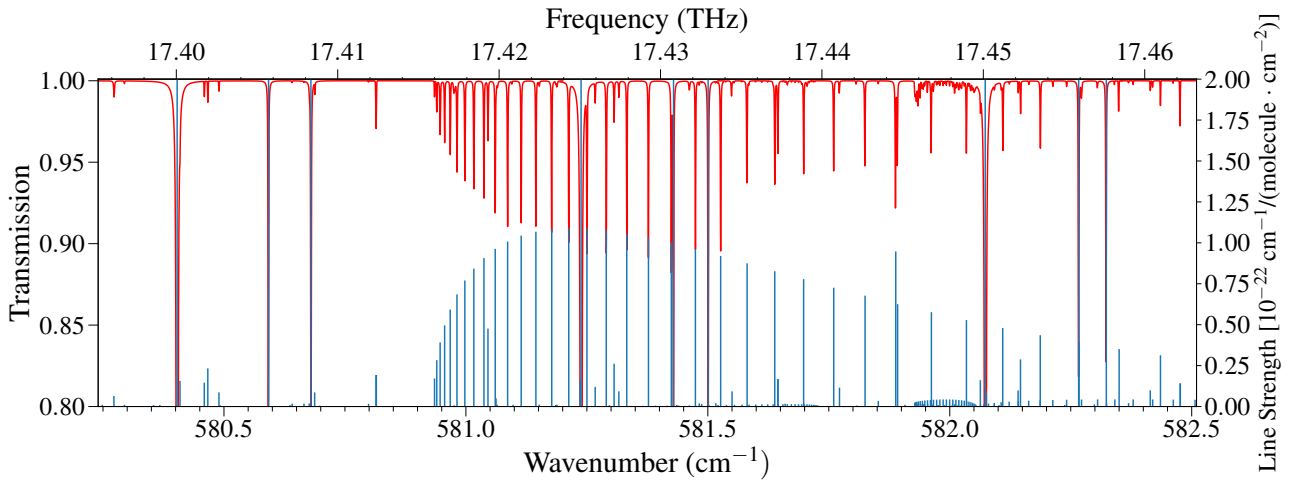


Figure 3.7: Comparison between our measured N_2O lines and the same empirical lines in the HITRAN [7] database.

central dip becomes deeper and broader as the optical depth increases. The high signal-to-noise ratio and the accurate modelling of the line profile allows us to find relative line centres with uncertainties below 10^{-4} cm^{-1} for almost all lines.

3.5 Data reduction

We have observed 165 N_2O lines in the frequency range from 580.40 to 582.48 cm^{-1} . Figure 3.7 shows the complete spectrum, where we have converted from the 2f modulation data back to the original absorption spectrum using the fitted Voigt parameters. In this figure, the red line is the new fitted absorption spectrum converted from the original wavelength modulated spectrum. For this dataset, the left hand axis gives the fraction of incident power transmitted through the cell. The blue sticks are the N_2O transitions from HITRAN [7] and are associated with the line strength given on the right axis. The strongest ν_2 lines are much stronger than the other lines, having an amplitude about 35 times the vertical scale of this figure.

Several strong lines, where the direct absorption is easily measured alongside the 2f data, are used to convert the amplitudes of the lines to the absolute transmission, thereby calibrating the vertical axis. We calibrate the frequency axis using cavity (built by Ge lenses) fringes as a 'ruler' and three calibration lines from the NIST database [36], namely the P(8), P(9) and

P(10) lines of the $(01^10) - (000)$ band of $^{14}N_2^{16}O$. The cavity data determines the frequency scale between each of the calibration lines. To treat the cavity data, we first remove the change in amplitude of the cavity fringes across the scans by normalizing the cavity data to the laser power. The power is determined from the baseline of the raw N_2O absorption spectrum. The resulting cavity fringes are almost sinusoidal because the cavity has such a low finesse. We apply a low-pass filter to the cavity data to remove higher order components, and then fit a sinusoidal model to segments of the spectral data. These segments typically contain 2-7 cavity fringes and are short enough that non-linearity in the conversion from QCL current to frequency is negligible. After piecing the segments together, a cavity phase can be assigned to every point in the scan. The phase difference between two calibration lines, whose frequencies are known, provides the conversion from phase to frequency. In this way, the frequency of every line in the spectrum is determined. The full list of measured frequencies is given in the second column of Tab. A.1.

Next we consider the uncertainties in determining the centre frequencies of all the lines. There are four main sources of statistical uncertainty (details in Sec. 3.7). The first comes from the calibration lines which each have a 1σ uncertainty of 1.5 MHz [26]. The second comes from the fits to the spectral lines. This uncertainty varies enormously between the weak and strong lines. It is about 2 MHz for the weakest lines that we have measured, and about 100 times smaller than this for the strongest lines. The third uncertainty comes from fitting to the cavity fringes and determining the cavity phase at each of the calibration lines and each of the lines of interest. This varies across the spectrum but is at most 0.4 MHz. The last source of uncertainty is due to the frequency drift of the cavity resulting from drifts of the laboratory temperature and pressure. We monitored these drifts by repeatedly scanning the same frequency region and measuring how the phase of the cavity changes with respect to an N_2O line over time. We also passed a 780 nm laser through the cavity and monitored how the cavity frequency changed relative to an atomic reference (a saturated absorption feature in Rb). The latter is more sensitive to the cavity drift because of the shorter wavelength. During an hour-long period of monitoring, we measured a linear cavity drift of 30 kHz/s at $17\ \mu m$. This uncertainty in the spectral line frequencies due to such a linear drift is tiny because the

calibration procedure almost perfectly eliminates the effect of the drift when both the drift and the frequency scan are linear in time. To produce a significant effect, the cavity length would need to change suddenly during the scan, or drift in one direction for part of the scan, and then the other direction for the rest. While monitoring the cavity, we did observe occasional sudden (few second) changes in the cavity frequency with amplitudes of about 5 MHz at $17\ \mu\text{m}$. We suppose that such changes may have been occurring while acquiring the N_2O data and include the effect as an uncertainty. The frequency uncertainty is largest for spectral lines that are far from a calibration line where they reach about 2.5 MHz. We note that, in most cases, the largest source of uncertainty comes from the calibration lines. The frequencies of these calibration lines were determined using a CO_2 laser as the reference [26]. Our observation suggests that a more accurate absolute reference will be useful in improving the accuracy of all the lines reported here to the sub-MHz level.

Collisions induce both a broadening and a shift of the spectral lines. To estimate this pressure shift, we note that HITRAN gives shift coefficients in air ranging from -15 to $+3$ MHz/atm for all lines in this region, while Toth [39] gives an average self-broadening shift coefficient of -45 MHz/atm for lines in the region $1800\text{--}2630\ \text{cm}^{-1}$. We did not find a value for the self-shift coefficients for our spectral region, but it should be similar to these values which give a negligible line shift for our operating pressure around 1 mbar. We add all uncertainties in quadrature to obtain the total uncertainty on each line. These are given in parentheses in the second column of Tab. A.1, where the number indicates the 2σ uncertainty in the last digits. For most lines, this is between 3 and 5 MHz. The root mean square (rms) value of the set of uncertainties is 3.6 MHz.

The absolute pressure of N_2O was not calibrated in the present work, so we are not currently able to report spectral line intensities on an absolute scale. Instead, Tab. A.1 (last column) gives the relative amplitude of each line in the spectrum which is the fitted value of the amplitude parameter of the Voigt function.

3.6 Molecular parameters

In the literature [39, 26], three different approaches have been used to model the rotational structure of the vibrational bands of N_2O . They differ in the way they treat the splitting of states with $l \neq 0$ into e and f levels, which we call the l -doubling. In the first approach [39] the e and f states are treated as separate vibrational states, each with their own term energy and set of rotational constants. This tends to introduce more parameters than are required. The second method [26], describes the energy using the empirical formula

$$E_v = G_v + B_v J(J+1) - D_v (J(J+1) - l^2)^2 + H_v (J(J+1) - l^2)^3 \\ \pm \frac{1}{2} q_v J(J+1) \mp \frac{1}{2} q_{vJ} J^2(J+1)^2 \pm \frac{1}{2} q_{vJJ} J^3(J+1)^3. \quad (3.3)$$

Here, the subscript v stands for the set of quantum numbers ν_1, ν_2, l, ν_3 , G_v is the term energy, B_v , D_v and H_v are rotational constants and q_v , q_{vJ} and q_{vJJ} are l -doubling constants (set to zero when $l = 0$). The third approach, used by Maki et al [26], includes matrix elements of the l -doubling Hamiltonian that couples states differing in l by 2 units. This is more consistent with molecule theory [46], but has the disadvantage that the wavenumbers of levels in one vibrational state depend on the parameters of a different vibrational state. We choose to use the second method and fit to our data using Eq. (3.3), because this method is consistent with the calibration lines [26].

We analyze those lines arising from the main isotopologue, $^{14}N_2^{16}O$. There is insufficient experimental data for the other isotopologues. For most of the vibrational states in our analysis, the rotational and l -doubling parameters have been established to high precision through microwave spectroscopy. The parameters are summarized in Table 1 of [26]. For the states (00^00) , (01^10) , (02^00) , (02^20) , (03^10) , (03^30) , (11^10) and (10^00) , we fix B_v , D_v , H_v , q_v , q_{vJ} and q_{vJJ} to the values given in [26], leaving only the G_v as free parameters. The rotational and l -doubling parameters for (04^20) and (12^00) are not provided in [26] so we leave them all as free parameters in our fits and determine them from our own data. We fit each band separately to Eq. (3.3). The output from these fits are the values of the band centre frequencies $\nu_0 = G_{v'} - G_v$, together

Band	ν_0 (cm ⁻¹)	Lines	χ_r^2
(01 ¹ 0) – (00 ⁰ 0)	588.76773(6)	3	1.5×10^{-4}
(02 ⁰ 0) – (01 ¹ 0)	579.36440(6)	2	20
(02 ² 0) – (01 ¹ 0)	588.97656(6)	6	5.4
(03 ¹ 0) – (02 ⁰ 0)	580.93263(5)	35	3.2
(03 ³ 0) – (02 ² 0)	589.16739(6)	6	11.9
(03 ¹ 0) – (02 ² 0)	571.32052(5)	6	5.9
(04 ² 0) – (03 ¹ 0)	582.05610(5)	51	2.9
(11 ¹ 0) – (10 ⁰ 0)	595.36234(6)	3	1.5
(12 ⁰ 0) – (11 ¹ 0)	581.73044(7)	21	0.72

Table 3.1: Band centre frequencies, in cm⁻¹, for nine vibrational bands of ¹⁴N₂¹⁶O.

with the rotational and l -doubling parameters for (04²0) and (12⁰0)¹.

Table 3.1 lists the values of ν_0 determined from the fits for nine vibrational bands of ¹⁴N₂¹⁶O, along with their uncertainties, the number in the parenthesis is the 1σ uncertainty in the last digits. The table also gives the values of the reduced chi-squared, χ_r^2 , which is the sum of the squared standardized residuals divided by the number of degrees of freedom in the fit. The values of χ_r^2 indicate reasonable fits. The uncertainties in the values of ν_0 are the quadrature sums of the uncertainties in the calibration lines and the errors returned by the fitting routine. Values of ν_0 for the first five bands in Tab. 3.1 are also given in [26]. Our values are consistent with [26] and are up to 20 times more precise.

From the ν_0 , we obtain the values of G_v for each of the vibrational states. The only information needed beyond Tab. 3.1 is the frequency of the v_1 mode, i.e. the value of G_v for (10⁰0). For this, we use the value given in Table 7 of [26].² Table 3.2 summarizes the parameters of nine vibrational states of ¹⁴N₂¹⁶O. Here, we present the values derived in the present work together with values given in Ref. [26]. In determining the uncertainties on the values of G_v we have added together the uncertainties on the contributing ν_0 in quadrature, assuming they are uncorrelated. The uncertainties on the parameters of (04²0) and (12⁰0) are those returned by the fitting routine. For (03¹0) we could determine two separate values of G_v , one from the analysis of the (03¹0) – (02⁰0) band and the other from the (03¹0) – (02²0) band. These two values were consistent within their errors, and we have taken their weighted mean.

¹ v' and v are the vibrational quantum numbers of the upper and lower states

²[26] has mistakenly swapped the v_1 and v_3 quantum numbers in Table 7 and in the associated spectral line assignments.

State	G_v	B_v	$10^7 D_v$	$10^{14} H_v$	$10^4 q_v$	$10^9 q_{vJ}$
(00 ⁰ 0)	0	0.4190109955(58)	1.76067(11)	-2.68(34)	—	—
(01 ¹ 0)	588.76773(6)	0.419573601(11)	1.78884(18)	-0.78(48)	7.9200575(38)	1.0205(60)
(02 ⁰ 0)	1168.13213(8)	0.419920179(20)	2.48083(41)	266.1(27)	—	—
(02 ² 0)	1177.74428(8)	0.420124871(15)	1.51161(37)	-134.1(31)	0.00374(31)	61.047(73)
(03 ¹ 0)	1749.06478(7)	0.420331000(30)	2.13767(81)	-19.0(73)	14.95159(21)	7.813(28)
(03 ³ 0)	1766.91168(10)	0.420663959(82)	1.5986(22)	-189(20)	—	—
(04 ² 0)	2331.12086(11)	0.42076842(24)	1.126(8)	-1380(9)	0.0109(37)	187(2)
(11 ¹ 0)	1880.26563(13)	0.417918418(16)	1.73355(24)	17.3(11)	9.08316(19)	-3.005(23)
(12 ⁰ 0)	2461.99606(15)	0.41814597(44)	2.394(11)	118(76)	—	—

Table 3.2: Molecular parameters of nine vibrational states of $^{14}N_2^{16}O$.

Figure 3.8 shows the result of fitting Eq. (3.3) to the Q branches of the (04²0) – (03¹0) and (12⁰0) – (11¹0) bands. In subfigure (a), Points: wavenumbers of lines in the Q-branch of the (04²0) – (03¹0) band; blue/red points have e/f symmetry in the lower level. Lines: fit to Eq. (3.3). (b) Points: wavenumbers of lines in the Q-branch of (12⁰0) – (11¹0); all points have f symmetry in the lower level. Line: fit to Eq. (3.3). Residuals are shown beneath each plot. These are the fits used to determine the parameters of (04²0) and (12⁰0) in Tab. 3.2. The numbers in the parentheses are the 1σ uncertainties in the last digits. All values are in cm^{-1} . The parameter q_{vJJ} is negligible for all states except for (02²0) where $q_{vJJ} = 2.755(60) \times 10^{-12} cm^{-1}$. All values of G_v , and all parameters for (04²0) and (12⁰0) are from the present work. All other values are from [26]. The reduced chi-squared values for these fits are given in Tab. 3.1. The (12⁰0) – (11¹0) data fit very well, with residuals all consistent with zero and no structure evident in the residuals (see Fig. 3.8). For the (04²0) – (03¹0) band, the points with e symmetry in the lower level are in blue and fit very well, while the points with f symmetry in the lower level are in red and show a slight deviation from the model around the turning point of the parabola indicating a minor failure of the model in this region, maybe this is because higher order parameters are not considered in the model.

3.7 Frequency error analysis

We record the N_2O spectrum and the cavity transmission simultaneously, giving two sets of data with a common abscissa. The abscissa may be the QCL current, or it may be time since the current is scanned linearly - we will call it t . The laser frequency is a function of t but

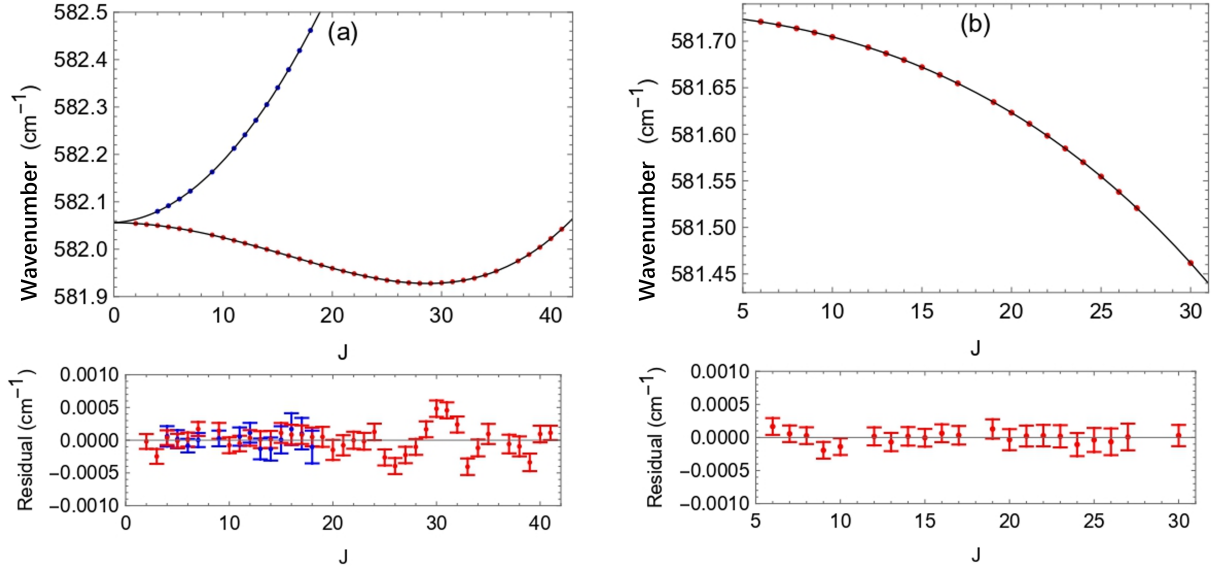


Figure 3.8: The result of fitting Eq. (3.3) to the Q branches of the $(04^2_0) - (03^1_0)$ and $(12^0_0) - (11^1_0)$ bands.

may not be a perfectly linear function. We fit to the cavity transmission data to get the cavity phase as a function of t , which is proportional to the laser frequency, $\phi(t) = \alpha f(t) + \theta$. We use three calibration lines, but for any line in the spectrum we only use the two closest calibration lines. They have frequencies f_i and corresponding cavity phases ϕ_i , with $\phi_i = \alpha f_i + \theta$. With these definitions, the frequency can be expressed as

$$f(t) = \frac{f_1(\phi_2 - \phi(t)) - f_2(\phi_1 - \phi(t))}{\phi_2 - \phi_1}. \quad (3.4)$$

From Eq. (3.4) we find the frequency uncertainty to be

$$\sigma_f = \sqrt{\sum_{i=1}^2 \left(\frac{\phi - \phi_i}{\phi_2 - \phi_1} \right)^2 (\sigma_{f_i}^2 + \beta^2 \sigma_{\phi_i}^2) + \beta^2 \sigma_{\phi}^2 + \beta^2 \left(\frac{d\phi}{dt} \right)^2 \sigma_t^2}, \quad (3.5)$$

where $\beta = \frac{f_2 - f_1}{\phi_2 - \phi_1}$. Here, σ_{f_1} and σ_{f_2} are the frequency uncertainties in the two calibration lines, σ_{ϕ_1} and σ_{ϕ_2} are the uncertainties in the cavity phases at the two calibration lines, σ_{ϕ} is the uncertainty in the cavity phase at the spectral line being measured, and σ_t is the uncertainty in determining the line centre of the spectral line on the t -axis.

In addition, we need to account for the uncertainty from the drift of the cavity's optical path

length, which arises due to changes in temperature and pressure. Let us first suppose that the cavity length drifts linearly in time at a rate γ , and the frequency is scanned linearly in time. Recognizing that the cavity phase is proportional to the frequency of the light multiplied by the length of the cavity, we find that Eq. (3.4) is modified to

$$f(t) = \frac{f_1(t_2 - t)(L + \gamma t_1) - f_2(t_1 - t)(L + \gamma t_2)}{(t_2 - t_1)(L + \gamma t)}, \quad (3.6)$$

where L is the nominal length of the cavity and $t_{1,2}$ are the times in the scan where the calibration lines appear. We treat the cavity drift as an uncertainty by assuming that its mean value is zero but its variance is not. This leads to a frequency uncertainty due to cavity drift of

$$\sigma_f = \frac{(f_2 - f_1)}{(t_2 - t_1)}(t - t_1)(t_2 - t)\frac{1}{L}\sigma_\gamma. \quad (3.7)$$

We monitored the frequency drift of the cavity and observed drifts up to 110 kHz/s. This translates to $\sigma_f < 2$ kHz, which is negligible. The uncertainty is tiny because the calibration procedure almost eliminates the effect of the drift when both the drift and the frequency scan are linear in time. The scan is not quite linear, but the non-linearity is small enough that the uncertainty remains negligible.

To produce a significant effect, the cavity has to drift in a different way. For example, suppose that in scanning from f_1 to f_2 , the cavity length expands linearly during the first half of the scan and then contracts linearly during the second half so as to return to its original length by the end of the scan. This conspiratorial behaviour produces a much larger effect. The uncertainty is

$$\sigma_f = \tau \left| \sigma_{\frac{df}{dt}} \right| \quad (3.8)$$

where $\frac{df}{dt}$ is the drift of the cavity resonance frequency and τ is the time to/from the nearest calibration line, i.e. $(t - t_1)$ or $(t_2 - t)$, whichever is smaller. A sudden step change in the length of the cavity part way through a scan has a similar effect.

3.8 Summary

Using a quantum cascade laser near $17\ \mu\text{m}$ and wavelength modulation spectroscopy, we have determined the frequencies of 165 vibrational transitions of N_2O . We have presented a model for the lineshape of absorption features in wavelength modulation spectroscopy, and used this model to fit our spectral data. An optical cavity is used to calibrate the relative frequency scale, and a few calibration lines of N_2O measured previously are used to fix the absolute frequency. This method transfers the accuracy of the calibration lines onto all other lines. From the data, we determine spectroscopic constants for seven vibrational states of N_2O . Ongoing work aims to build a frequency standard in this spectral region based on the fundamental vibrational transition in trapped, ultracold CaF molecules [3]. Standards of this kind could be developed throughout the mid-infrared using the vibrational transitions of a wide range of laser-cooled molecules [30]. These standards can then be used to improve the precision of large sets of spectral lines in common gases such as N_2O , using the methods described in the present work.

Chapter 4

Driving the fundamental vibrational transition of CaF

The CaF clock will be built by a Raman system to drive the $(v, N, v', N') = (0, 0, 1, 0)$ transition of CaF as a clock. The design of this experiment is shown in Fig. 4.1[3]: the yellow and green arrows indicate the lasers for cooling and detection of the CaF molecules. The grey arrow indicates the 17.5 THz clock transition which has the sensitivity $K_\mu = 0.5$ to fundamental constant μ . The red arrows are two Raman lasers for driving the $(v, N, v', N') = (0, 0, 1, 0)$ transition. The 17 μm laser can be used to drive the transition between $(v, N) = (0, 1)$ and $(v, N) = (1, 0)$ states (blue), which is dipole allowed. Because the clock transition is electric dipole forbidden and has never been driven before, we wanted to make a first measurement by driving a closely-related transition. We start by driving the $(v, N, v', N') = (0, 1, 1, 0)$ transition. This transition is electric dipole allowed and can be driven by the 17 μm laser. The frequency difference between this transition and the desired clock transition is just a rotational spectroscopic constant, which has been accurately measured by microwave spectroscopy at the kHz level [5]. Meanwhile, using the future accurate experimental frequency data of CaF, N₂O transition frequencies can be calibrated by driving and comparing the transitions of the two molecules at the same time.

The procedure for driving the $(v, N, v', N') = (0, 1, 1, 0)$ transition has several steps:

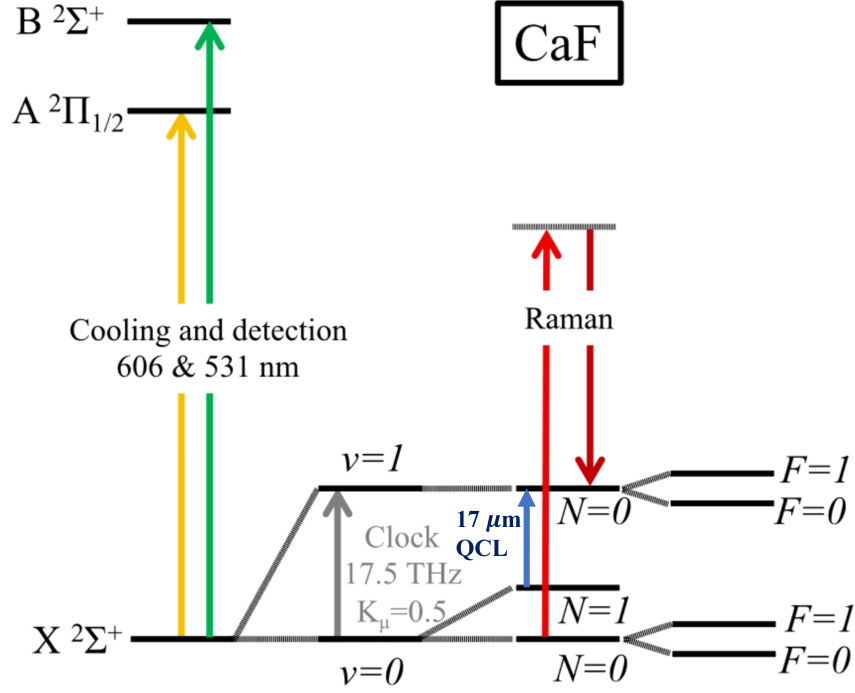


Figure 4.1: Modified from Fig. 1.4. Relevant energy levels of CaF. From [3].

- Cooling of CaF molecules** CaF molecules are produced by chemical reaction between a Ca vapour produced by laser ablation of a Ca target and SF_6 gas that flows over the target. These molecules then thermalize to 4K through collisions with cold helium gas, and form a beam moving at about 150 m/s. Then the molecules are laser slowed, cooled and trapped in a Magneto-Optical Trap (MOT) and further cooled to a few μK level [5].
- Preparation of 17 μm laser** The 17 μm laser frequency is calibrated by N_2O absorption spectroscopy, details are presented in Chapter 3. There are several N_2O lines whose frequencies are close to the target $(v, N, v', N') = (0, 1, 1, 0)$ transition of CaF. By performing absorption spectroscopy of N_2O around these lines, the correct frequency range for driving the CaF transition is found.
- Driving the CaF $(v, N, v', N') = (0, 1, 1, 0)$ transition** After CaF molecules are cooled and trapped, the molecules will be left in free space for about 10 ms to interact with the 17 μm laser. The transition will be driven in this period.
- Detection of the transition** The transition is detected by the loss of molecules which are captured in a second MOT. When the 17 μm laser is at the transition frequency,

CaF molecules are driven to the $(v, N) = (1, 0)$ state, which is not in the cycle of laser cooling, so the detected molecule number will be smaller than the case when no transition happens.

The details of the above steps will be presented in later sections of this chapter.

4.1 Introduction to laser cooling

Laser cooling is a technique which uses laser to 'cool' atoms and molecules to low temperatures such as mK, μ K or even nK level. The mechanism of laser cooling is energy transfer from atoms or molecules to laser photons. The development of laser cooling and trapping contributes significantly to many areas in AMO physics [47], e.g. searching for variation of fundamental constants [3], parity violation [48], etc., precision tests of quantum electrodynamics [49], study of quantum degenerate gases and applications like quantum information [50] and computation [51]. The theoretical background of laser cooling and detailed setup of the laser cooling experiment has been presented in [5]. Here is a brief introduction to those theories.

4.1.1 Doppler cooling

The Doppler cooling of atoms and molecules is based on the Doppler effect. Using a laser with frequency tuned slightly lower than the transition used for laser cooling, the molecules in the laser beam will absorb photons when they move towards the laser source according to the Doppler effect. Then these molecules will scatter photons in random directions. The net result of the absorption and emission is the molecules are slowed. The Doppler cooling process can

be described using a two-level system. The optical Bloch equations are written as:

$$\frac{\partial \rho_{ee}}{\partial t} = i\frac{\Omega}{2}(\tilde{\rho}_{eg} - \tilde{\rho}_{ge}) - \Gamma\rho_{ee} \quad (4.1)$$

$$\frac{\partial \rho_{gg}}{\partial t} = -i\frac{\Omega}{2}(\tilde{\rho}_{eg} - \tilde{\rho}_{ge}) + \Gamma\rho_{ee} \quad (4.2)$$

$$\frac{\partial \rho_{ge}}{\partial t} = -\left(\frac{\Gamma}{2} + i\delta\right)\tilde{\rho}_{ge} - i\frac{\Omega}{2}(\rho_{ee} - \rho_{gg}) \quad (4.3)$$

$$\frac{\partial \rho_{eg}}{\partial t} = -\left(\frac{\Gamma}{2} - i\delta\right)\tilde{\rho}_{ge} + i\frac{\Omega}{2}(\rho_{ee} - \rho_{gg}) \quad (4.4)$$

where $|e\rangle$ and $|g\rangle$ are the excited and lower states in a two-level system, separated by energy $\hbar\omega_0$, interacting with the electromagnetic field of a laser $\epsilon E_0 \cos(\omega_0 + \delta)t$. In the above equations, $\rho_{ij} = \langle i|\varphi\rangle\langle\varphi|j\rangle$ are the matrix elements of the density operator with $\tilde{\rho}_{ge} = \tilde{\rho}_{eg}^* = \rho_{ge}e^{-i\omega_0 t}$. $\Omega = -\langle g|\vec{d}\cdot\vec{\epsilon}|e\rangle E_0/\hbar$ is the Rabi frequency and $\Gamma = \omega_0^3 |\langle g|\vec{d}|e\rangle|^2 / (\pi\epsilon_0\hbar c^3)$ is the rate of spontaneous emission from the excited state.

The scattering rate is written as $R_{sc} = \Gamma\rho_{ee}^{st}$, ρ_{ee}^{st} is the steady-state excited state population, which can be found from Eq. 4.4:

$$R_{sc} = \Gamma \frac{\Omega^2/\Gamma^2}{1 + 4\delta^2/\Gamma^2 + \Omega^2/(2\Gamma^2)} = \frac{\Gamma}{2} \frac{I/I_s}{1 + 4\delta^2/\Gamma^2 + \Omega^2/(2\Gamma^2)} \quad (4.5)$$

where $I = \epsilon_0 c E_0^2/2$ is the intensity of the laser field and the saturation intensity is defined as:

$$I_s = \frac{c\epsilon_0\Gamma^2\hbar^2}{4|\langle g|\vec{d}\cdot\vec{\epsilon}|e\rangle|^2} \quad (4.6)$$

The force exerted by a laser beam with wavevector $\vec{k}$ parallel to the velocity v of the beam is:

$$\vec{F}_{rad} = \hbar\vec{k}R_{sc} \quad (4.7)$$

The limitation of the Doppler cooling is the heating due to fluctuations of the cooling force,

the heating rate of a 3D cooling system with six beams is:

$$\frac{d\langle v^2 \rangle_{fluc}}{dt} = 2R_{sc} \left(\frac{\hbar k}{m} \right)^2 \quad (4.8)$$

Then the temperature of the steady state can be found when the cooling and heating mechanisms reach an equilibrium:

$$T_D = -\frac{\hbar \Gamma^2}{8k_B \delta_0} (1 + 4\delta_0^2/\Gamma^2 + I/I_s) \quad (4.9)$$

4.1.2 Magneto-optical Trap

The cooling technique which cools neutral atoms and molecules to the level of μK is called optical molasses [52]. A magneto-optical trap (MOT) provides confinement for the cooled atoms and molecules by adding a quadrupole magnetic field gradient to the optical molasses [52]. In experiments, the MOT is usually created by adding a pair of coils to generate a quadrupole $\mathcal{B}$ field, applying it to an optical molasses. An atom positioned near the field zero may experience transitions of $F' = F + 1$, where F' and F are the total angular momentum of the upper and lower state. Two circularly polarised, counter-propagating laser beams with the same handedness are used to drive transitions which push the molecules to the centre of the MOT.

4.1.3 Sub-Doppler cooling

In experiments, the atoms and molecules can be cooled much lower than the Doppler limit. There are several methods of sub-Doppler cooling, including Sisyphus cooling [53], evaporative cooling [54], Raman sideband cooling [55], etc. The mechanism of the Sisyphus cooling [53] is introduced here, as it is most relevant to the techniques we use to cool the molecules.

Using two counter-propagating laser beams with orthogonal polarization to irradiate on the molecules, a gradient between three polarizations σ^- (left-handed circular polarization), π

(linear polarization) and σ^+ (right-handed circular polarization) is generated along the standing wave. When the molecules are moving through the standing wave, they will lose kinetic energy when 'climbing' towards the potential maximum; then the molecules will be pumped to a lower energy state, and climb the potential hill again. The molecules continuously lose kinetic energy during this process, and can be cooled to micro-kelvin level [5].

4.2 Experimental laser cooling setup

In this section, the laser cooling setup for driving the CaF fundamental vibrational transition will be briefly introduced. The schematic diagram is shown in Fig. 4.2.

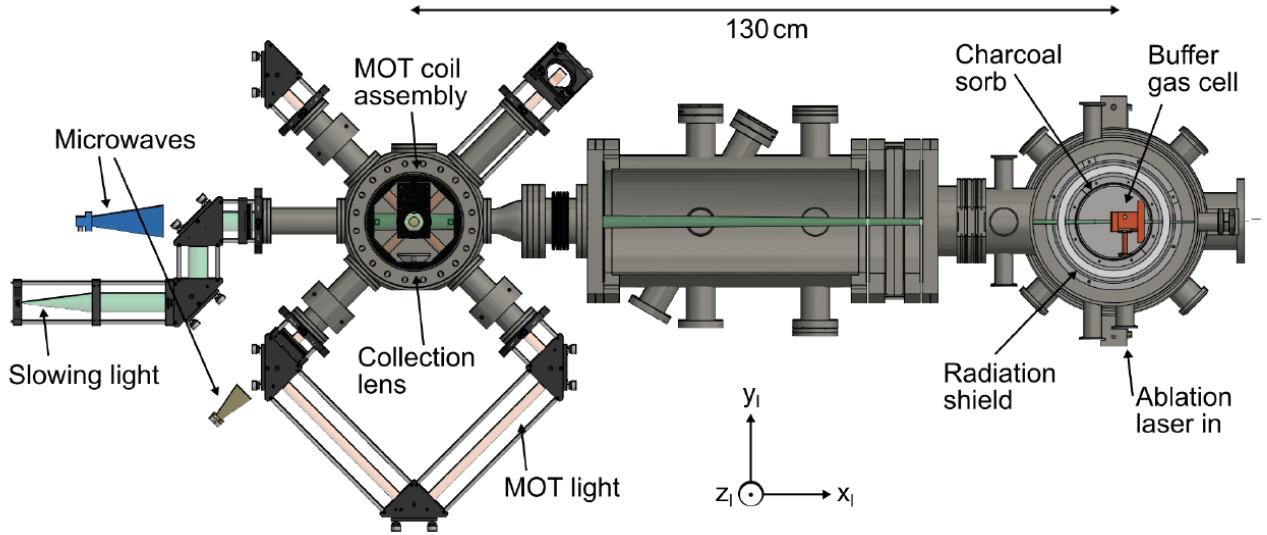


Figure 4.2: Schematic diagram of the laser cooling experiment. From [5].

4.2.1 Source

The chamber on the right in Fig. 4.2 is the source. It consists of a copper cell which is cooled to 4K by a cryocooler. Inside this buffer gas cell, there is a Ca rod; SF_6 gas and cold helium gas both flow through the cell. Using a Nd:YAG laser to ablate the Ca target, CaF molecules are produced by the reaction between Ca atoms and SF_6 gas. The CaF molecules are flushed out of the exit aperture of the cell by the flow of helium gas, forming a molecular beam.

4.2.2 Laser cooling

The theoretical background of laser cooling and detailed setup of the experiment has been presented in [5] and briefly introduced in the previous section. Lasers used for this experiment are drawn in red and green in Fig. 4.2, they are used to drive different transitions in the laser cooling cycle shown in Fig. 4.3: the wavelengths and branching ratios are marked on the transitions. The solid lines are the transitions driven by the MOT lasers, the dashed lines are the transitions driven by the slowing lasers. The notation for the MOT lasers follows the rule: the laser driving the transition $A^2\Pi_{1/2}(v = j, J = 1/2) - X^2\Sigma^+(v = i, N = 1)$ is denoted by $\mathcal{L}_{ij}$ with $ij \in \{00, 10, 21, 32\}$. $\mathcal{L}_{00}$ is the main cooling laser, the other lasers which drive vibrational transitions with $v > 0$ lower state are used for repumping, because the CaF molecules in the $A^2\Pi$ state can go to different vibrational levels on the ground electronic states according to the vibrational branching ratio. The green 531 nm laser $\mathcal{L}_{00}^s$ which drives the $B^2\Sigma^+(v = 0, N = 0) - X^2\Sigma^+(v = 0, N = 1)$ transition is used to slow the molecular beam from the source. Another slowing laser is the red repump laser $\mathcal{L}_{10}^s$.

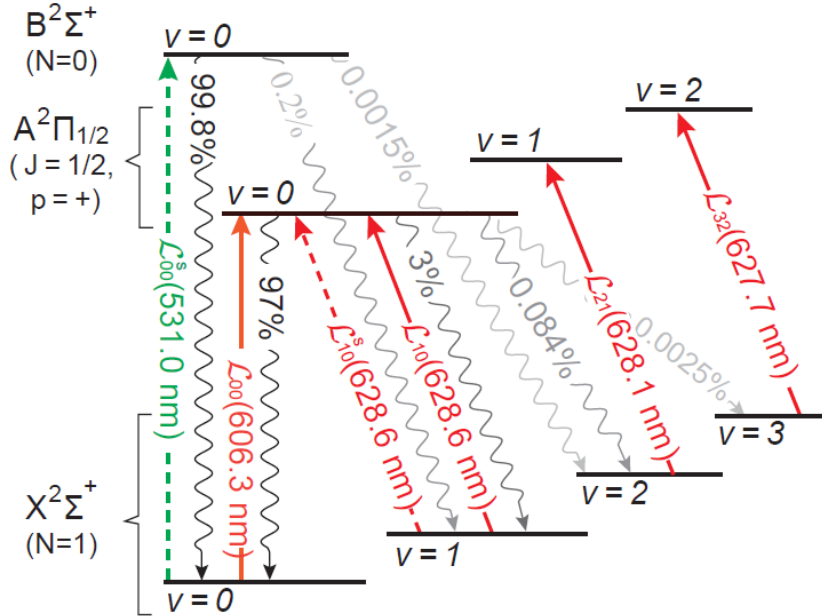


Figure 4.3: The laser cooling cycle for CaF. From [5].

The magnetic field for making the MOT is set up by two pairs of rectangular coils, they can generate a roughly uniform magnetic field in the chamber. This field is perpendicular to the axis

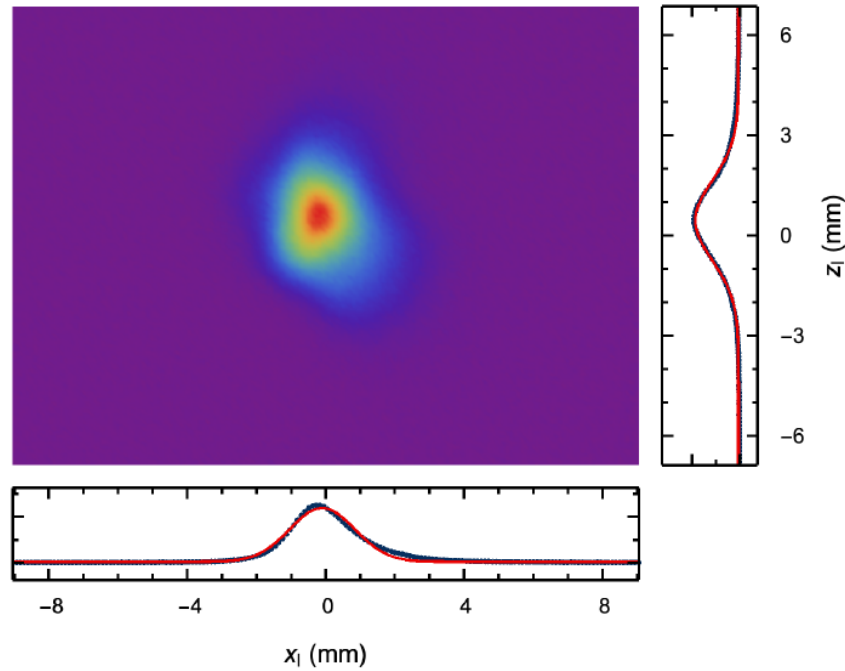


Figure 4.4: A single shot fluorescence image of MOT with an exposure time of 10 ms. From [5].

of the molecular beam. Another three pairs of shim coils around the MOT chamber are built for precision control of the magnetic field. The MOT signals are captured by a CCD camera with a focusing lens to collect the fluorescence. A typical MOT fluorescence image is shown in Fig. 4.4. The sequence of the experiment is controlled by a custom software MOTMASTER developed by CCM group members at Imperial Collge London [5].

4.3 Injection lock for the v2 and v3 MOT lasers

The slowing laser, the main cooling laser, and the first repump laser (addressing $v = 1$) are all commercial laser systems. The two repump lasers addressing $v = 2$ and $v = 3$, labelled L_{21} and L_{32} (v2 and v3) in Fig. 4.4 are homebuilt diode laser systems consisting of a "seed" laser and an amplifier. The stability of these homebuilt systems needed to be improved in order to make the subsequent experiments feasible. In this section, I will describe the work I did to improve their stability. The MOT seed lasers are locked to a multi-channel wavemeter with the accuracy at the MHz level during the experiment. For the lasers driving the $v = 2 \rightarrow 1$ and

$v = 3 \rightarrow 2$ transitions, the seed cannot provide enough power for making the MOT, so light from a frequency-stabilized 'seed' is amplified using a higher power diode. The light from the seed laser is sent into the amplifier which forces it to run at the same frequency as the seed. This is known as injection locking. The seed and amplifier are often called the master laser and the slave laser respectively [56].

4.3.1 Injection lock

Injection locking [56] is a widely used technique when locking one semiconductor laser to another. A 'slave' laser is locked to the 'master' laser by injecting the master laser light to the diode of the slave laser. The injection locking setup in our experiment is shown in Fig. 4.5. By injecting the master laser beam into the slave laser diode, the frequency of the slave laser follows the master laser. The slave laser frequency is monitored using a Fabry-Perot cavity. The signal received on a photodiode is sent to the relocker box, the relocker box will automatically relock the slave laser when it leaves the locking window (see Fig. 4.6).

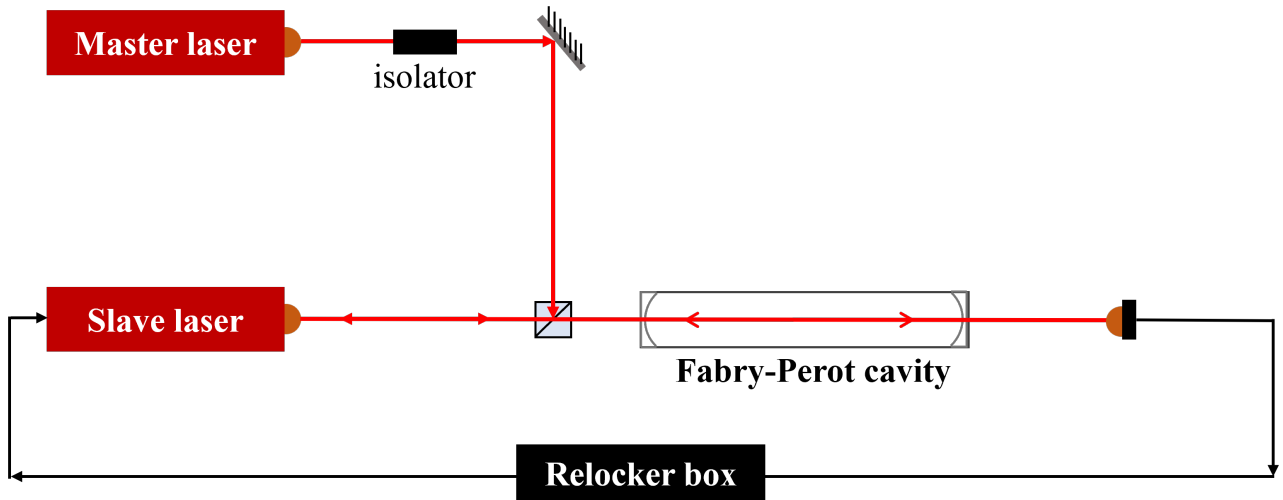


Figure 4.5: The injection locking setup in our experiment.

In the experiment, the light from the v_2 and v_3 seed lasers is sent to the diodes of the slave lasers. When the frequencies of the master and slave lasers are close to each other, the frequencies of the slave lasers will follow the master lasers with a fixed phase offset. This frequency synchronization only works when the frequencies of the master and slave lasers are close enough

(around 10 MHz level). If the frequency difference is too big, the slave laser will unlock, meaning that it no longer runs at the frequency of the master. Fig. 4.6 shows the locking window of the v3 laser: the x axis is the output voltage (dimensionless) to the v3 slave laser, which controls the current of the slave laser. This value is linearly proportional to the free-running laser frequency. The units of the y axes are also dimensionless. The blue dots are the measured Fabry Perot peak value and indicate whether or not the slave laser is outputting a single laser mode - only then is the output high. The red dots show the position of the peak measured on the Fabry-Perot cavity, which is equivalent to frequency. When the DAC outputs a value from Arduino (the microcomputer which control the relocker) that is between 250 and 400, the slave laser is stably locked to the master laser, because the Fabry Perot peak amplitudes and positions are stable, which means the output frequency and power of the slave laser is not changing with the input voltage. It is synchronized with the master laser. The frequency of the master laser is fixed, and the frequency of the slave laser will follow it provided the current provided to the slave laser is within an acceptable range. The aim is to find this range. To do this, the light from the slave laser is sent to a scanning Fabry-Perot cavity ($\text{FSR} = 1.25 \text{ GHz}$, linewidth $\approx 3 \text{ MHz}$, tuning rate at the hundred Hz level) which acts as a spectrum analyzer of high resolution. When driving the piezo on one of the mirrors in the cavity, the cavity length oscillates, so the FSR also oscillates. This is equivalent to scanning the frequency of the laser, so the transmission peak of the laser through the cavity can be found. This peak is used to check the mode and frequency of the slave laser. When the laser is injection-locked it will output a single stable mode, so the spectrum analyzer will show a tall peak that is stable in frequency and amplitude. When the laser is not injection-locked it is likely to run on multiple modes and at a frequency different to the master laser. In Fig. 4.6, the region where the peak amplitude (blue) and the peak position (red) are stable is the injection locking window.

4.3.2 Injection relockers

If the slave laser is manually parked in the injection locking window, it can stay locked for several minutes to hours, depending on the drift of the master laser, room temperature drift

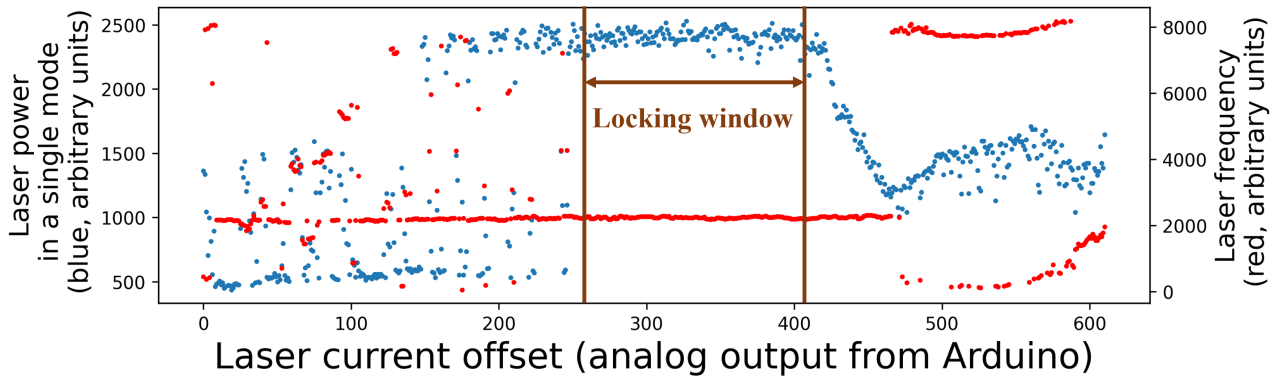


Figure 4.6: The locking window of the v3 laser.

and some other disturbance. The vibrational spectroscopy experiment requires stable operation for several hours, so I built a re-locking device to drive the v2 and v3 slave laser back to the locking window within one to several seconds. The scheme of the relocker is shown in Fig. 4.7: the "Ain" ports are analog inputs, one of them receives the transmission signal after the Fabry-Perot cavity, the other receives the trigger of the cavity signal. The "Dout" port is a digital output, LED indicators are connected to show the status of the locking. The "DAC" port outputs control current to the slave laser for relocking. The Arduino Due (microcomputer) is connected to a computer and charged via a USB cable, commands can also sent from the computer to control the relocker. The Arduino script I wrote for relocking is presented in Appendix B.

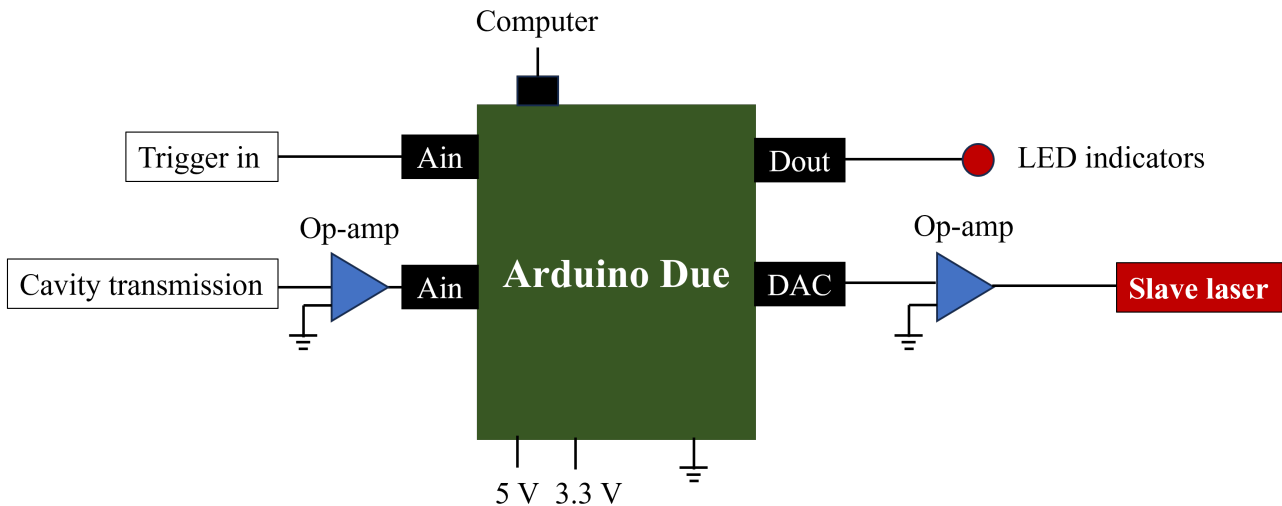


Figure 4.7: The scheme of the injection relockers for v2 and v3 slave lasers.

The injection relockers continuously receive the signal from the photodiode which records the

transmission of the slave laser beam through the scanning Fabry-Perot cavity. Using this information, the relockers will first record a full locking window, then park the laser at the centre of the window. When unlock events are detected from the transition peak amplitude and position, the relockers will try to relock the laser by moving its frequency for half a window in both directions. If this fails, the relocker will continuously change the output voltage to scan around to find the full locking window and park the laser to the centre again. The long-term stability of the slave laser with the re-locker activated was tested over a two day period. The laser remained injection locked throughout this period with no human intervention needed. Without the re-locker, human intervention is typically needed every hour.

Fig. 4.8 shows a 3.5 hour long segment of the data which shows the peak values (read from Arduino, dimensionless) recorded during the scans of the slave laser beam through the scanning Fabry-Perot cavity, it was recorded over two days where two re-locking events occurred. The y axis is the peak transmission value (dimensionless) of the slave laser beam through the scanning Fabry-Perot cavity, the value is read from the analog input of Arduino. This is a section of a long test during a weekend for the injection relocker. The laser can stay locked for 15 min to several hours depending on the strength of environmental disturbance. There were two relock events that happen when $t = 18.5hr$ and $t = 20.8hr$. The first one is a fast relock which only moved the output voltage from the Arduino for half a width of the locking window. In the second relock event, the locking window was rescanned, so it takes a few seconds. The peak position drifts because the temperature in the lab drifts. This is a drift of the Fabry-Perot cavity used to monitor the laser, not a drift of the laser frequency itself.

4.4 Target CaF transition and comparison with N₂O

The CaF $(v, N, v', N') = (0, 1, 1, 0)$ transition is driven by the same 17 μm laser as for the N₂O spectroscopy. The position of this transition can be determined from the N₂O lines which are close to the CaF transition. In this section, the basic properties (estimated position, linewidth, hyperfine structure) of this transition are discussed, the frequency comparison between this CaF

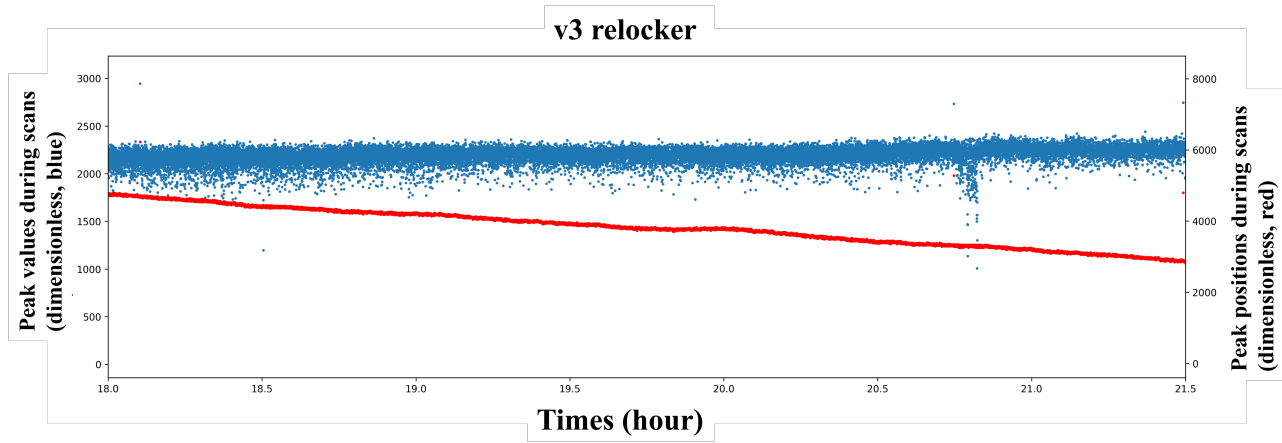


Figure 4.8: A section of a long test during a weekend for the injection relocker.

transition and N_2O lines is also presented.

4.4.1 CaF $(v, N, v', N') = (0, 1, 1, 0)$ transition in the $X^2\Sigma^+$ state

Hyperfine structure

For CaF, the nuclear spin quantum number $I = 1/2$. For its ground electronic state $X^2\Sigma^+$, $S = 1/2$, so the possible value of $F = N + S + I$ for the $N = 0$ state is 0 and 1; for the $N = 1$ state, F can be 0, 1 or 2. The hyperfine structure of the CaF $(v, N, v', N') = (0, 1, 1, 0)$ rovibrational transition is shown in Fig. 4.9. On the left, the centre transition frequency of hyperfine splittings from $v = 0, N = 1$ to $v = 1, N = 0$ state is 17.45 THz. The colored lines on the right are the hyperfine splittings of this rovibrational transition. In this figure, the frequency values of the hyperfine levels are the deviations from the centre frequency. This figure shows the relative frequencies between the transitions, their linewidths and intensities are related with the transition dipole moment, they are introduced in later paragraphs.

Transition dipole moment

The vibrational modes of diatomic molecules come from the oscillation of the bond length between atoms. The electronic dipole moment $\mu(R)$ can be expanded in a Taylor series about

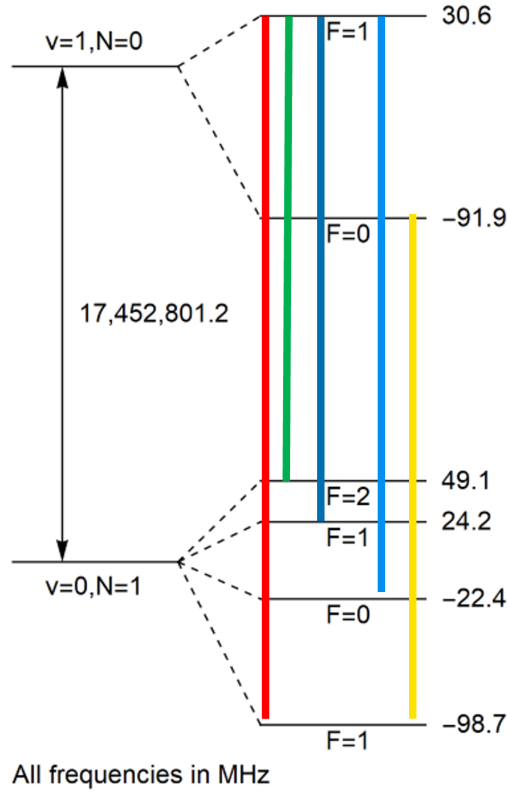


Figure 4.9: Hyperfine structure of CaF $(v, N, v', N') = (0, 1, 1, 0)$ transition of the $X \ ^2\Sigma^+$ state.

the equilibrium bond length position:

$$\mu(R) = \mu(R_e) + \frac{\partial \mu}{\partial R}(R - R_e) \quad (4.10)$$

where $\mu(R) = \langle \phi_{ei} | \mu | \phi_{ei} \rangle$ is the electronic dipole moment integral.

The vibrational dipole moment integral can be written as:

$$\langle \phi_{\nu f} | \mu(R) | \phi_{\nu i} \rangle = \mu(R_e) \langle \phi_{\nu f} | \phi_{\nu i} \rangle + \frac{\partial \mu}{\partial R} \langle \phi_{\nu f} | R - R_e | \phi_{\nu i} \rangle + \dots \quad (4.11)$$

$$= \frac{\partial \mu}{\partial R} \langle \phi_{\nu f} | R - R_e | \phi_{\nu i} \rangle + \dots \quad (4.12)$$

The first term in Eq. 4.11 vanishes because different vibrational modes are orthogonal.

Using $\hat{x} = \sqrt{\hbar/2m\omega}(a^\dagger + a)$ operator in the harmonic oscillator approximation, which is quite

suitable to describe the $v = 0 \rightarrow v = 1$ transition:

$$\langle \phi_{\nu f} | R - R_e | \phi_{\nu i} \rangle = \langle 0 | \hat{x} | 1 \rangle \quad (4.13)$$

$$= \sqrt{\frac{\hbar}{2m\omega}} (\sqrt{2} \langle 0 | 2 \rangle + \langle 0 | 0 \rangle) \quad (4.14)$$

$$= \sqrt{\frac{\hbar}{2m\omega}} \quad (4.15)$$

then the vibrational dipole moment can be written as:

$$\langle \phi_{\nu f} | \mu(R) | \phi_{\nu i} \rangle = \sqrt{\frac{\hbar}{2m\omega}} \frac{\partial \mu}{\partial R} \quad (4.16)$$

where m is the mass of the CaF molecule, ω is the transition frequency, $\partial \mu / \partial R$ is the derivative of the dipole moment function evaluated at $R = R_e$, which can be calculated by taking the derivative of the dipole moment vs. R curve from the dipole moment curve of the CaF ground electronic state shown in Fig. 4.10 [8], where R is the internuclear distance, $M(r)$ is the linear fit to the dipole moment data.

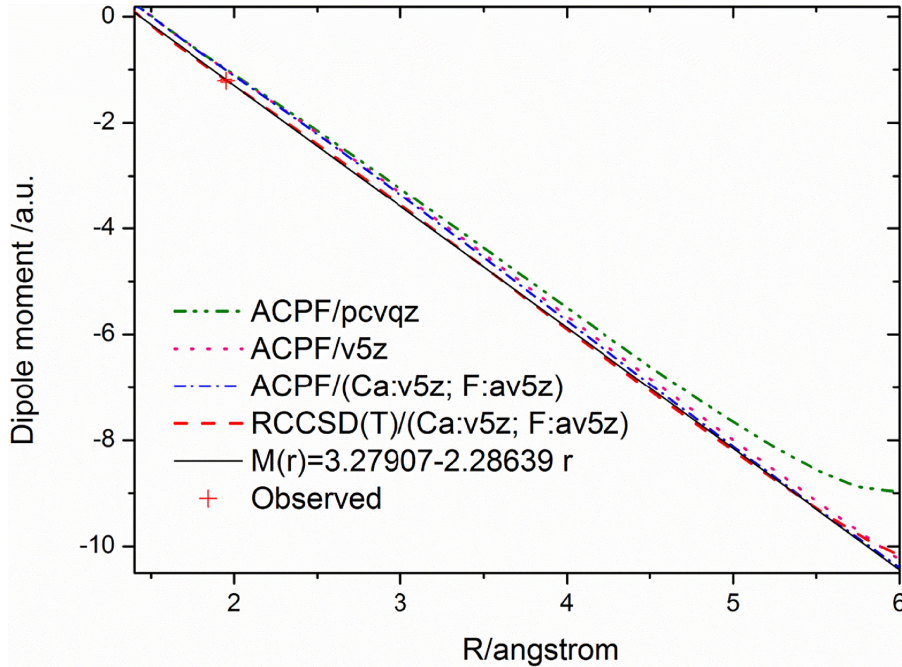


Figure 4.10: Dipole moment of CaF in the linear range from ACPF and RCCSD(T) calculations (ACPF and RCCSD(T) are ab initio calculation methods.) from [8].

Considering the transitions to individual hyperfine levels, the final transition dipole moment

transition((F, F'))	relative strength
(0, 1)	1.57
(1 ⁺ , 1)	3.13
(1 ⁻ , 1)	1.57
(2, 1)	7.83
(1 ⁺ , 0)	1.57
(1 ⁻ , 0)	3.13

Table 4.1: The relative strengths between different hyperfine transitions of CaF (v', N', v, N)=(1,0,0,1) transition.

can be written as:

$$\begin{aligned}
& \langle v; \Lambda, N; S, J, I, F, m_F | T_p^1(\mu) | v'; \Lambda, N'; S, J', I, F', m'_F \rangle \\
&= \langle v; \Lambda, N; S, J, I, F, m_F | \mathcal{D}_{pq}^{(1)}(\omega)^* T_q^1(\mu) | v'; \Lambda, N'; S, J', I, F', m'_F \rangle \\
&= \langle v, \Lambda | T_q^1(\mu) | v', \Lambda' \rangle \langle N; S, J, I, F, m_F | \mathcal{D}_{pq}^{(1)} | N'; S, J', I, F', m'_F \rangle \\
&= \sqrt{\frac{\hbar}{2m\omega}} \frac{\partial \mu}{\partial R} (-1)^{F'+F-m_F+J+J'+S+2N+I-\Lambda} \\
&\quad \times \sqrt{(2F+1)(2F'+1)(2J+1)(2J'+1)(2N+1)(2N'+1)} \\
&\quad \times \begin{Bmatrix} J' & F' & I \\ F & J & 1 \end{Bmatrix} \begin{Bmatrix} N' & J' & S \\ J & N & 1 \end{Bmatrix} \begin{pmatrix} N & 1 & N' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} F & 1 & F' \\ -m_F & p & m'_F \end{pmatrix}
\end{aligned}$$

where $T_p^1(\mu) = \mathcal{D}_{pq}^{(1)}(\omega)^* T_q^1(\mu)$ is the transformation from space-fixed to molecule-fixed coordinate systems. The relative strengths calculated based on the above equations between different hyperfine transitions are presented in Tab. 4.1.

Linewidth

In a two-level system, the rate of spontaneous emission between an excited state $|e\rangle$ and a ground state $|g\rangle$ is:

$$\Gamma = \frac{\omega_0^3 | \langle g | d | e \rangle |^2}{3\pi\epsilon_0 \hbar c^3} \quad (4.17)$$

The time to reach a steady state is $1/\Gamma$, for the CaF $(v, N, F) = (0, 1, 0) \rightarrow (1, 0, 1)$ transition, this is about 200 ms with $\omega_0 = 2\pi \times 17 \times 10^{12}$ rad/s, $| \langle g | d | e \rangle | = 1.94 \times e^{-19}$.

The saturation intensity is written as:

$$I_S = \frac{\pi c h \Gamma}{3 \lambda^3} \quad (4.18)$$

The linewidth of the transition between the two levels is:

$$\gamma = \Gamma \sqrt{1 + I/I_S} \quad (4.19)$$

Using the result above, the linewidths of hyperfine transitions of CaF fundamental vibrational transition can be estimated. For the hyperfine transition we are particularly interested in, the linewidth-power relation is shown in Fig. 4.11: the calculated saturation intensity of this transition is $1.928 \times 10^{-10} \text{ W/m}^2$. The total power of the $17 \text{ }\mu\text{m}$ QCL is $\approx 1 \text{ mW}$, which gives a linewidth of hundreds of kHz. Actually, the transition can be further broadened to the level of MHz because the laser has a linewidth of this scale.

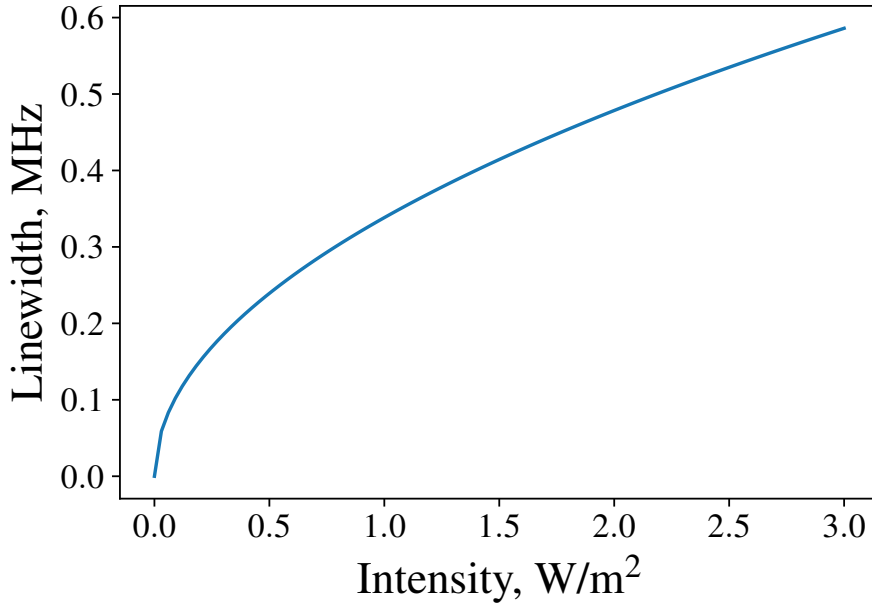


Figure 4.11: The linewidth of CaF $X^2\Sigma^+ (v, N, F) = (0, 1, 0) \rightarrow (1, 0, 1)$ transition.

From the estimation of linewidth in Fig. 4.11, the hundreds of kHz linewidth of the hyperfine transitions are not hard to observe in our experiment. Since the frequency differences between hyperfine transitions are much larger than their linewidths, the hyperfine splitting should also be easily observed in our experiment.

Interaction time

In this experiment, it is important to know how long the molecules need to interact with the 17 μm to drive the transition efficiently. We would also like to understand the conditions necessary to drive coherent Rabi oscillations. To study the possibility of observing coherent processes in this system, the optical Bloch equations have been solved numerically [57]:

$$\frac{\partial \rho_{ee}}{\partial t} = i\frac{\Omega}{2}(\tilde{\rho}_{eg} - \tilde{\rho}_{ge}) - \Gamma\rho_{ee} \quad (4.20)$$

$$\frac{\partial \rho_{gg}}{\partial t} = -i\frac{\Omega}{2}(\tilde{\rho}_{eg} - \tilde{\rho}_{ge}) + \Gamma\rho_{ee} \quad (4.21)$$

$$\frac{\partial \tilde{\rho}_{ge}}{\partial t} = -(\gamma + i\Delta)\tilde{\rho}_{ge} - i\frac{\Omega}{2}(\rho_{ee} - \rho_{gg}) \quad (4.22)$$

$$\frac{\partial \tilde{\rho}_{eg}}{\partial t} = -(\gamma - i\Delta)\tilde{\rho}_{eg} + i\frac{\Omega}{2}(\rho_{ee} - \rho_{gg}) \quad (4.23)$$

The symbols are defined as:

$$\rho_{ij} = \langle i|\phi\rangle\langle\phi|j\rangle \quad (4.24)$$

$$\tilde{\rho}_{ge} = \tilde{\rho}_{eg}^* = \rho_{eg} \exp(-i\omega_0 t) \quad (4.25)$$

$$\Omega = -\langle g|d \cdot \epsilon|e\rangle \frac{E_0}{\hbar} \quad (4.26)$$

$$\Gamma = \frac{\omega_0^3 |\langle g|d|e\rangle|^2}{3\pi\epsilon_0 \hbar c^3} \quad (4.27)$$

where ρ_{ij} are the matrix elements of the density operator, Ω is the Rabi frequency, and Γ is the rate of spontaneous emission from the excited state. The numerical solutions to the optical Bloch equations are solved with $\omega_0 = 2\pi \times 17 \times 10^{12}$ rad/s, $|\langle g|d|e\rangle| = 1.94 \times 10^{-19}$. From the simulation, the coherent process is hard to discover in the current setup, but it is possible when the laser power is at 10 mW level and the noise level is lower than 100 kHz, which is available for our second-generation 17 μm QCL. Fig. 4.12 shows the lineshape of the CaF transition with different interaction times: the X axis is the detuning from the line center in MHz, the Y axis is ρ_{ee} from the optical Bloch equation, which describes the population of molecules in the upper state of a transition. In the left figure, all of the parameters are from the real experiment with 1 mW laser power and 1cm^2 area; in the right figure, the light intensity has been raised

to 10 times the current case, and the linewidth is half that of the current laser. At normal power and linewidth (left figure) the simulations suggest that the transition is saturated for all interaction times between 0.5 ms and 5 ms. The linewidth grows with increasing interaction time, reaching the MHz level for $t = 5$ ms. The excited state population is never higher than 0.5 and there are no indications of coherent processes. This is because the laser linewidth is too large compared to the Rabi frequency. However, when we implement the laser with higher power and have better control of the interaction time, the coherent process appears. The first indication of this can be seen in the small dip at the centre of the line for the $t = 0.1$ ms case in the right hand figure.

Coherent control of a quantum system is important in AMO physics and can be applied to the study of quantum information [50]/computation [51]. If appropriate laser power (at the level of 10 mW) and interaction time (< 1 ms) is chosen in the experiment, the coherent process may appear. In our experiment, coherent process was not observed because the laser power is only at 1 mW level and the interaction time was not controlled very well.

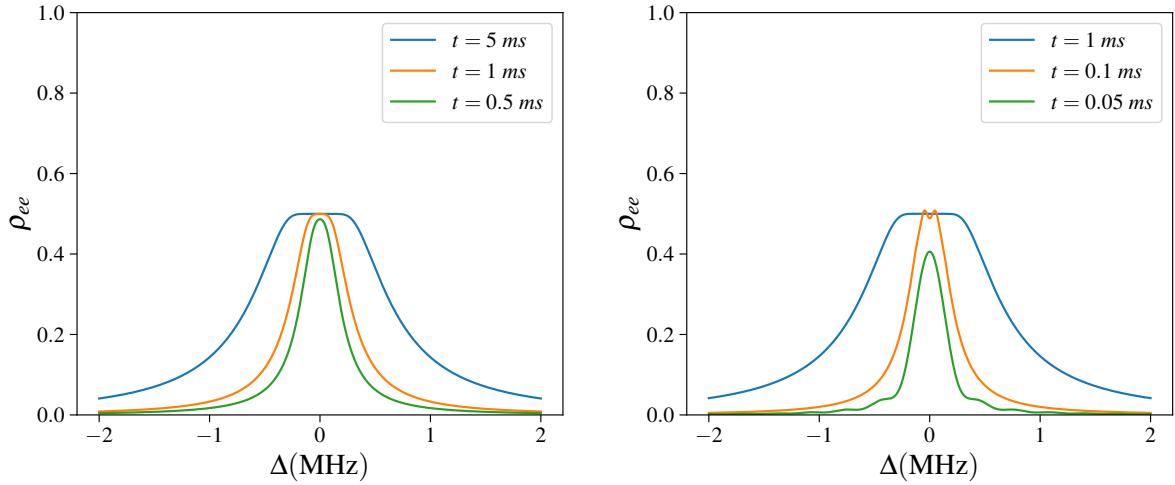


Figure 4.12: The simulated lineshape of the CaF $(v, N, v', N') = (0, 1, 1, 0)$ transition for different interaction times.

4.4.2 Comparison between N₂O and CaF transitions

The $(v, N, v', N') = (0, 1, 1, 0)$ transition from the ground electronic state of CaF is close to several N₂O lines in frequency. The closest N₂O line is predicted to be the $X^1\Sigma^+ (v_1 v_2^l v_3) =$

$(03^10) \rightarrow (04^20)$ $Q9e$ transition of $^{14}N_2^{16}O$ at 582.163 cm^{-1} . The predicted positions of CaF transitions and N_2O transitions are shown in Fig. 4.13: in the upper figure, the horizontal blue line is a part of the N_2O spectrum, it is the demodulated WMS signal strength at $2f_{mod}$. The N_2O transitions from left to right on this figure are: $^{14}N_2^{16}O$ $(02^20) \rightarrow (03^10)$ $R12e$, $^{14}N^{15}N^{16}O$ $(00^00) \rightarrow (01^10)$ $R7e$, $^{14}N_2^{16}O$ $(03^10) \rightarrow (04^20)$ $Q9e$ and $^{14}N_2^{16}O$ $(02^00) \rightarrow (03^10)$ $Q32e$. The colored vertical lines are the predicted frequencies of CaF $(0, 1, 0) \rightarrow (1, 0, 1)$ hyperfine transitions, from left to right they are: (a) $F = 1^+ \rightarrow 0$, (b) $F = 2 \rightarrow 1$, (c) $F = 1^+ \rightarrow 1$, (d) $F = 1^- \rightarrow 0$, (e) $F = 0 \rightarrow 1$ and (f) $F = 1^- \rightarrow 1$. In the lower figure: the frequency range around $^{14}N_2^{16}O$ $X^1\Sigma^+ (v_1v_2^lv_3) = (03^10) \rightarrow (04^20)$ $Q9e$ transition is zoomed in to show the hyperfine splittings of CaF transition more clearly. In the experiment, the $17 \mu\text{m}$ laser is first parked around the $^{14}N_2^{16}O$ $X^1\Sigma^+ (v_1v_2^lv_3) = (03^10) \rightarrow (04^20)$ $Q(9e)$ transition. Then we scanned the laser around this central frequency with a step size of 100 kHz to search for the CaF transitions.

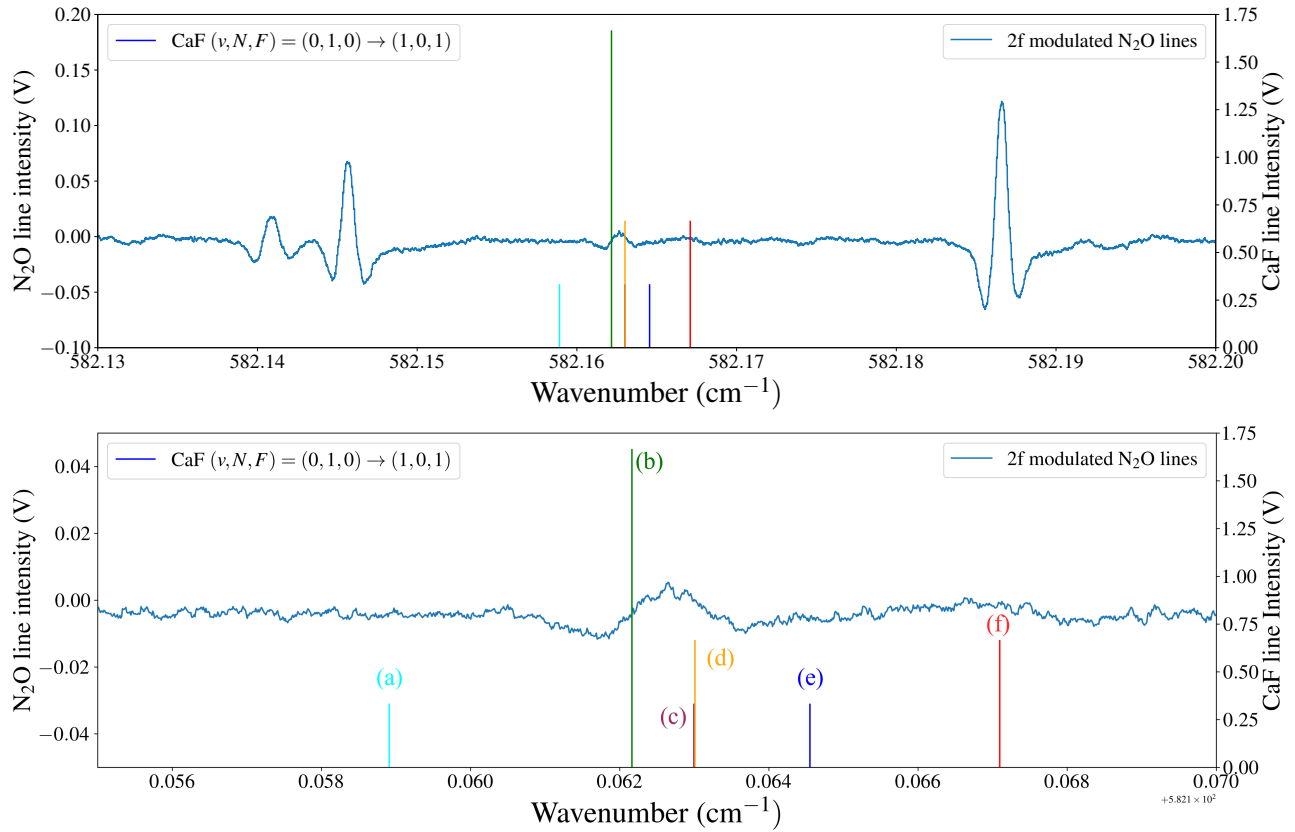


Figure 4.13: Predicted frequencies of the CaF $(v, N) = (0, 1) \rightarrow (1, 0)$ hyperfine transitions compared with N_2O lines.

4.5 Noise measurement

The CaF vibrational transition has a natural linewidth of just a few Hz from calculation. When measured in free space, the actual linewidth is likely to be dominated by Doppler broadening. For example, at a temperature of 100 μ K, the Doppler broadened FWHM is about 16 kHz. If the linewidth of the laser is broader than this, the measured transition linewidth will be dominated by the laser linewidth and the laser will be less efficient at driving the transition. Therefore, it is important to study the frequency noise of the laser. In this section, different sources of noise in this experiment are measured using a HP 3562a FFT spectrum analyzer.

The laser noise measurement is performed using the ν_2 P(8) transition of N₂O as a frequency discriminator. The laser is first parked on the slope of one side of the P(8) line, then a current control box is activated to give a feedback to the laser to lock it to the initial set point. The result of the measurement is presented in Fig. 4.14.

The noise measured on the side of the transition has several sources:

- The frequency noise of the laser, which is the noise we would like to measure.
- The power change of the laser. Since the power of the 17 μ m QCL changes with the frequency, so the measured 'frequency noise' always contains the amplitude change on the recorded signal. To distinguish the frequency and power fluctuation of the laser, another measurement is done in a frequency range where there is no transition. The comparison between the two measurements gives the pure frequency noise.
- The noise of the MCT detector and its preamplifier. They can be measured when the laser is blocked.
- The noise of the spectrum analyzer itself. This noise is measured when the input of the spectrum analyzer is terminated using a 50 Ω resistor.

The measured noise in different cases is shown in Fig. 4.14, where different sources of noise are marked with different colors. The blue line shows the total laser noise, and includes the

laser frequency noise because this measurement was made on the slope of the spectral line. The red line reflects the laser amplitude noise, which is measured at a frequency where no N_2O transition is seen. The orange line is mainly the noise from the preamplifier and the MCT detector, which is measured when the laser is blocked. The green line shows the noise only from the spectrum analyzer, where the whole experimental setup is disconnected from the spectrum analyzer and the spectrum analyzer is terminated by a $50\ \Omega$ resistor.

From the noise measurement result shown in Fig. 4.14, the dominant noise in our experiment is the laser frequency noise, and it is at the $10^9\ \text{Hz}^2/\text{Hz}$ level at 1 Hz. All the other sources of noise have little influence on the frequency measurements. The expected linewidth of the CaF vibrational transition is around 1 MHz, the laser linewidth is smaller than 100 kHz as expected, so it will not limit the accuracy of the CaF transition frequency measurement.

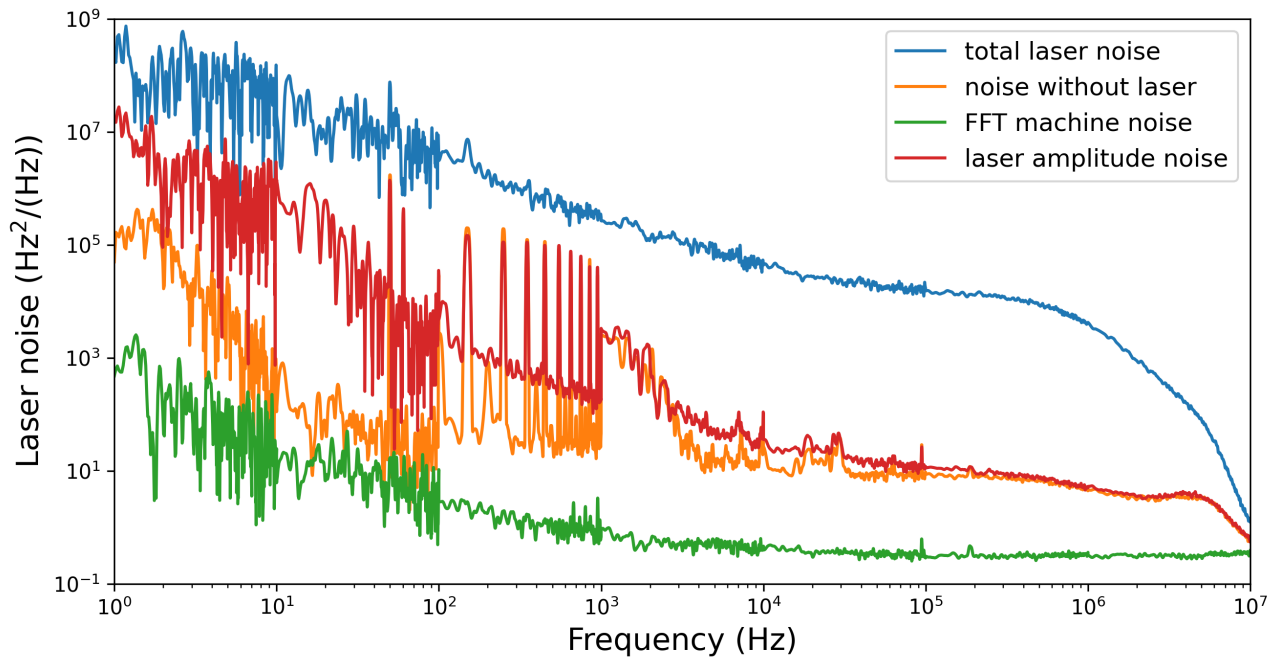


Figure 4.14: Different kinds of measured noise in this experiment.

4.6 The experimental set-up

The experimental set-up for driving the CaF $(v, N, v', N') = (0, 1, 1, 0)$ transition combines the N₂O spectroscopy setup described in Chapter 4 with the apparatus used to produce ultracold CaF described in this chapter (Fig. 4.2). A beamsplitter is used to send about half the 17 μm laser power to the CaF apparatus and half to the N₂O spectroscopy setup. The two setups are on separate optical tables and a periscope is used to transfer the 17 μm light to the CaF apparatus.

4.6.1 Alignment

The alignment and collimation of the beam is calculated and optimized for the distance between the optical tables: at the centre of the chamber, the 17 μm laser beam is at its waist (w_0) which is chosen to be $w_0 = 1$ cm. The procedure of alignment is:

- **Alignment of a 531 nm laser with the 17 μm laser:** because the 17 μm laser is infrared and no beam card for invisible lasers can cover this frequency region, another visible laser is used for optical alignment instead. A 531 nm laser beam is delivered from a fibre to the N₂O experiment as the reference for the alignment. A flip mirror is used to switch between the 531 nm and 17 μm beams. The MCT detectors have an area of only 0.1 mm, so they serve as precise targets for alignment. The detectors are optimized for the 17 μm region, but they can also detect visible light with a small sensitivity. This feature is used for the alignment. An iris is placed before the N₂O gas cell. The distance between this iris and the MCT detector is approximately 0.5 m, and together they define the beam path with high accuracy.
- **Alignment of the 531 nm laser to the CaF chamber:** the 531 nm laser is delivered from the N₂O experimental setup to the MOT chamber using a periscope built with mirrors. These mirrors are attached to optical posts with 2 inch diameter for the best stabilisation. The rough alignment can be done by observing the reflection from the

chamber window. However, the position of the molecules depends on the directions of the MOT lasers, it is often not exactly positioned at the centre of the chamber. The precise alignment is done by 'blowing away molecules'. The frequency of the 531 nm laser is tuned to match the $B\ ^2\Sigma^+ - X\ ^2\Sigma^+$ transition of CaF, so the molecules in the MOT are pushed out of the trap by the radiation pressure of the resonant 531 nm laser. By observing the disappearance of CaF molecules on the CCD camera, the alignment of the 531 nm laser is confirmed. Since the 531 nm and 17 μm laser have already been aligned in the previous step, the 17 μm laser is also now aligned to the trapped molecules.

4.6.2 Sequence of the experiment

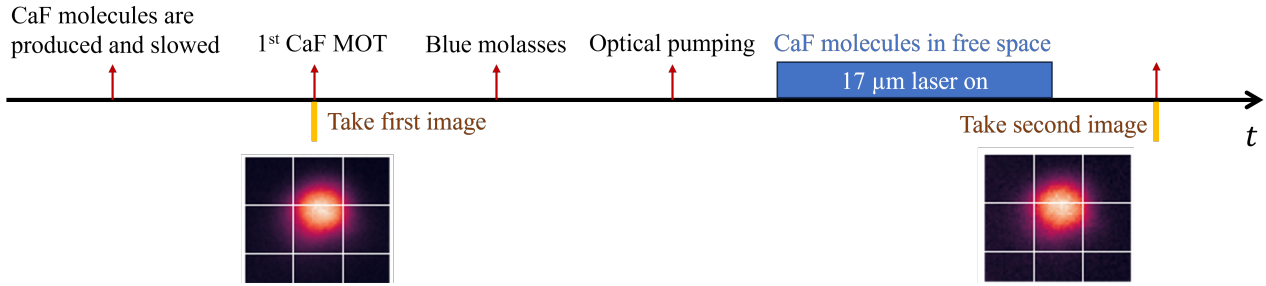


Figure 4.15: Sequence of the experiment of driving the CaF $(v, N, v', N') = (0, 1, 1, 0)$ transition.

The sequence for this experiment is shown in Fig. 4.15. The sequence control is done by the lab computer using the software MOTMaster (written in C#) with python scripts for input and output. A pulse of CaF molecules is produced by the cryogenic source. After the slowing, the CaF molecules are trapped in a MOT and a first image is taken to record the molecule number. Next the magnetic field is turned off and the frequency of the cooling laser is stepped to form a blue-detuned optical molasses. This cools the molecules to about 50 μK , as described in [5]. This step of cooling allows more interaction time between the molecules and the 17 μm laser because the colder cloud expands more slowly. All of the lasers are turned off after the cooling steps. The CaF molecules experience free fall for 5-10 ms. This period is left for the interaction between CaF molecules and the 17 μm laser. When the 17 μm laser drives the vibrational transition of CaF, the molecules will be pumped to the state $(v, N) = (1, 0)$ which is not in the cooling cycle shown in Fig. 4.3. The 2nd MOT is made after driving the CaF vibrational

transition, and the 2nd image is taken during this MOT. If transitions happen in the previous step, the molecules pumped to the $(v, N) = (1, 0)$ state are not re-captured; which means less molecules can be observed in the 2nd image than in the case when no transition happens.

4.6.3 CaF transition measurement

The measurement of the CaF $(v, N, v', N') = (0, 1, 1, 0)$ transition is done by comparison between the molecule number during the first and second MOT described in Sec. 4.6.2. Before putting CaF molecules into the MOT, images for background light at the time of MOTs are taken. These background images are used to subtract the influence of light that does not come from the molecules. The molecule number in the MOT is determined from the counts recorded on the CCD camera as shown in Fig. 4.16. The ratio r_1 between the MOT numbers in the two images reflects the loss of molecules during this period. Because the molecules lost between images can also be from the decay in the MOT and other cooling steps, the depth of the transition is the ratio r_2 between different r_1 s when the transitions happen ($r_1(trans)$) or not ($r_1(bg)$):

$$r_1 = \frac{N_{MOT2}}{N_{MOT1}} \quad (4.28)$$

$$r_2 = \frac{r_1(trans)}{r_1(bg)} \quad (4.29)$$

where N_{MOT1} and N_{MOT2} are the molecule numbers in the 1st and 2nd MOTs. Fig. 4.17 shows the relation between the parameters.

4.7 Result

Fig. 4.18 shows the result of the experiment described in section 4.6.2 which aimed to find the CaF vibrational transition and its hyperfine splittings. The vertical bars at the bottom of the plot are the calculated positions of the hyperfine transitions, the blue dots are the measured lines and the red curve is the Gaussian fit to the lines. Fig. 4.9 shows the states associated with the

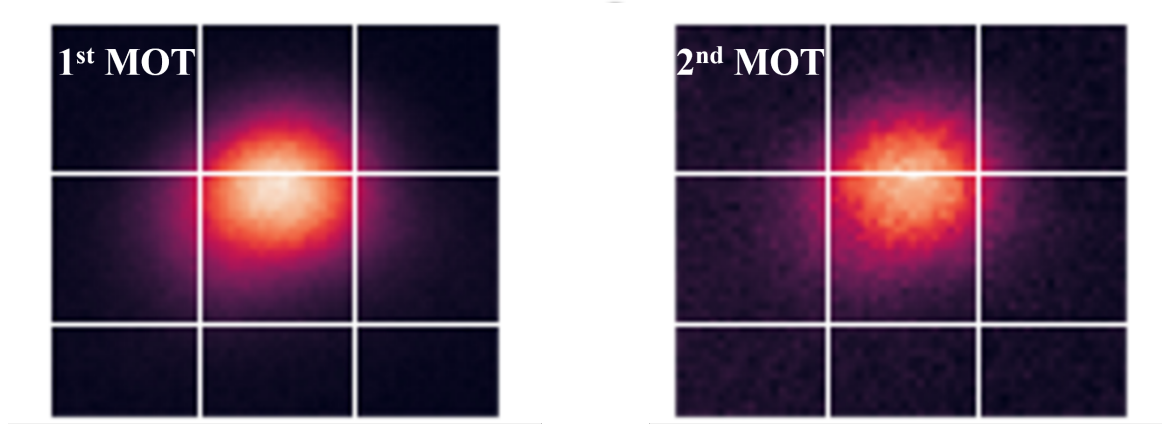


Figure 4.16: Images taken in the first and second MOT in the sequence described in Sec. 4.6.2.

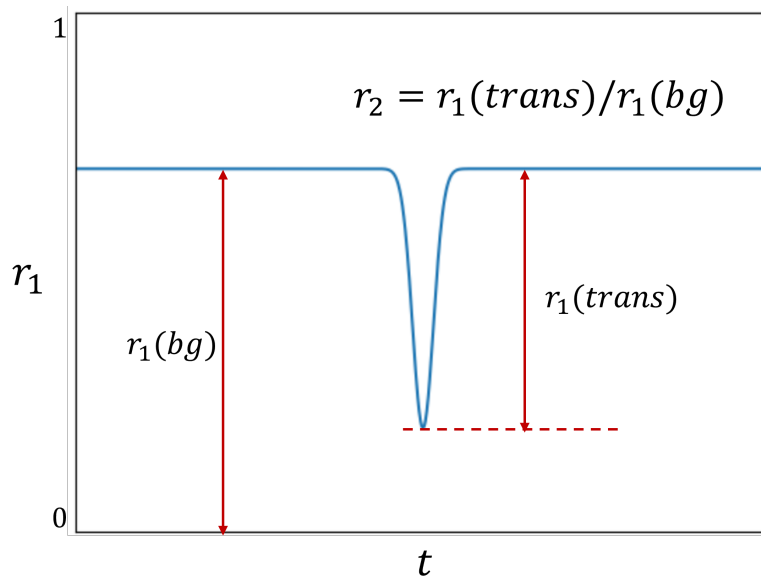


Figure 4.17: The definition of ratios in Eq. 4.29. The y axis is the ratio r_1 of molecule number taken from the images of two MOTs. The depth of the transition is $r_2 = r_1(trans)/r_1(bg)$.

transitions, the colors used to mark different hyperfine transitions is consistent with the vertical bars in Fig. 4.18, which means that we've found the target CaF transitions. The linewidths of the measured lines are around 5-10 MHz, which is consistent with the calculations when the laser power is at mW level, and the frequency intervals are consistent with the calculated hyperfine structure to within 5 MHz. The strongest transition in Fig. 4.18 is actually two overlapped transitions with the frequency difference much smaller than their linewidths.

Although the experiment was successful, there are still several problems that need to be addressed.

- **The frequency calibration** In this experiment, the relationship between the frequency and temperature and current settings of the laser is measured first. Then the CaF transitions are measured in a separate experiment. However, the laser frequency is slowly drifting at a rate of more than 10 MHz per hour. The measurements of CaF transitions usually takes 30 min, so the determination of the laser frequency is limited by this drift. The frequency uncertainty is at the level of 10 MHz and cannot be determined accurately because the drift speed is not constant, so no accurate frequency data can be provided for now. The solution to this problem is to scan the N₂O and CaF lines at the same time. To do such an experiment, a laser with more power is needed, a faster switch with switching time smaller than 1 ms is required and the control over the two sides of the experiment (CaF and N₂O) should be synchronized.
- **Laser frequency control** A shutter was used in this experiment to block the 17 μ m laser to the CaF experiment when the MOT and molasses are being made, so that the 17 μ m laser does not influence the trapping and cooling of the molecules. A problem was that the speed of the shutter is not fast enough (using 10 ms to fully block the laser), so the molecules interact with the 17 μ m laser during the molasses period. We tried to jump the laser frequency so that it is not resonant during this period, but the frequency response of the laser was too slow. A new laser from MirSense has been ordered, and electronics are being built to implement a fast switch for the frequency control. The new current controller will also solve the problem of the frequency stability of the laser, since it can be controlled using a computer. It gets rid of the noise which is introduced by the function generator driving the laser and the BNC cables connecting the equipments. We scanned the CaF spectrum many times, very different lineshapes and linewidths were observed each time, and sometimes the lines were much noisier than anticipated, even hard to distinguish the line centre. We attributed this to noise on the laser current driver arising from the method used to control the laser directly from the computer. The amplitude of this noise is around 20 mV, it corresponds to 500 kHz frequency of the laser. The typical linewidth of the observed CaF lines is 1-5 MHz, the electronic noise is apparently one of the dominating errors in the frequency measurement. A new current controller has been

built that is controlled from the computer through serial commands rather than direct control, and features very low noise which is much smaller than the laser linewidth.

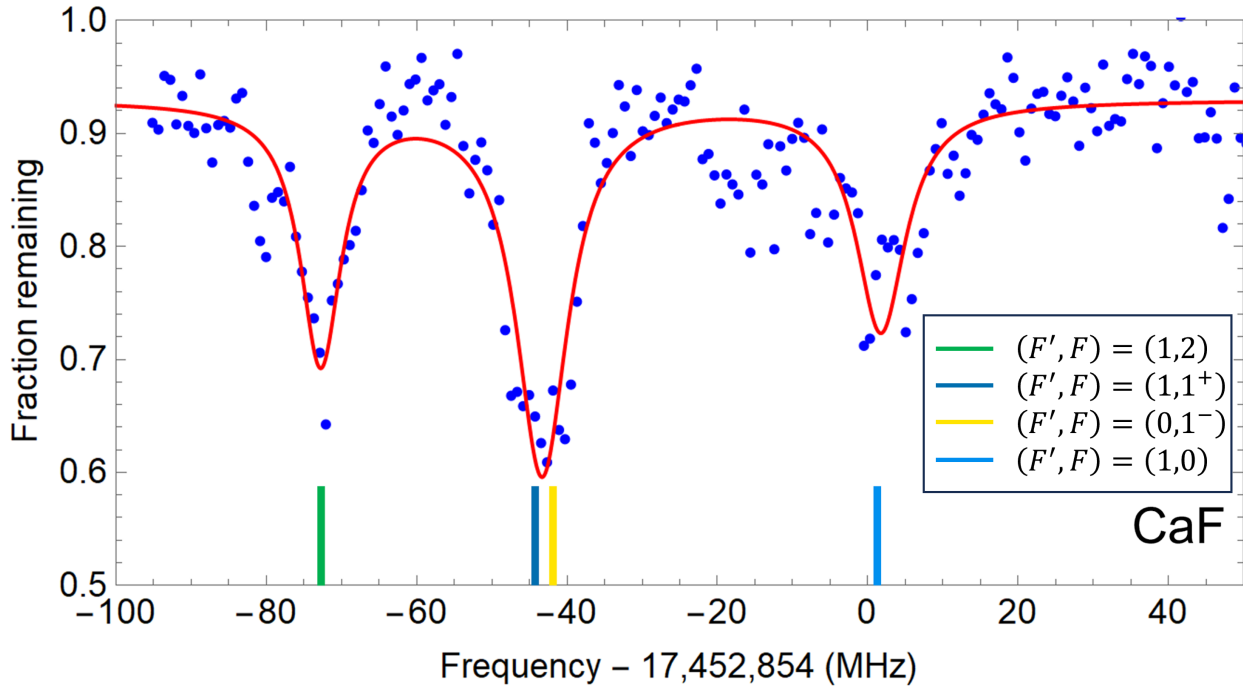


Figure 4.18: The measured CaF hyperfine transitions (blue dots) compared with calculated result.

4.8 Summary

This chapter introduces the experiment of driving the fundamental vibrational transition of CaF. This experiment is a preliminary experiment for making the clock, the frequency information obtained from the result will help to build the Raman system for the clock. The theory of the technique required for this experiment – laser cooling, is introduced, and the laser cooling setup in the lab is also presented. The stability of the cooling lasers is important, so the injection lock setup for two lasers is presented. The theories and experimental setup for driving the CaF vibrational transition are described. Finally, the result of this preliminary experiment is presented, and possible improvements for this experiment are also discussed.

Chapter 5

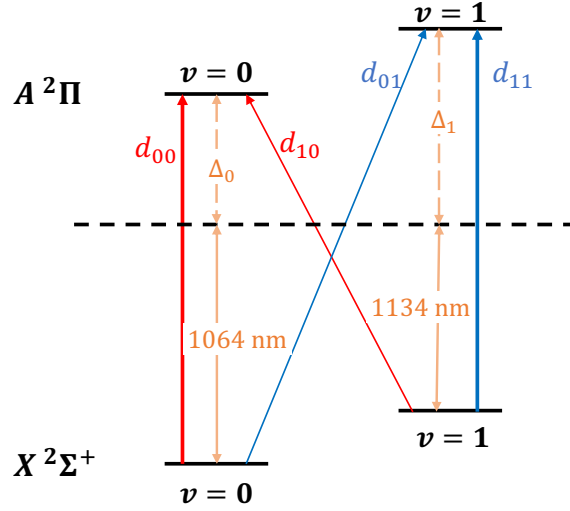
A Raman system for driving the CaF clock transition

In Chapter 4, the experiment for driving the vibrational transition at $17\text{ }\mu\text{m}$ was described. The $17\text{ }\mu\text{m}$ experiment verifies the frequency of the CaF fundamental vibrational transition which was first measured in our experiment described in Chapter 4. For building a molecular clock, the systematic uncertainties need to be controlled and minimized. The $(v, N, v', N') = (0, 0, 1, 0)$ transition as a clock is better than the $(v, N, v', N') = (0, 1, 1, 0)$ transition because the Stark shift and Zeeman effect are the smallest when the rotational state does not change in the transition and is chosen to be $N = 0$. To build such a clock using the electric dipole forbidden $(v, N, v', N') = (0, 0, 1, 0)$ transition, a Raman system which drives a two-photon transition is essential. In this chapter, the design of the clock experiment and the built set-up will be presented.

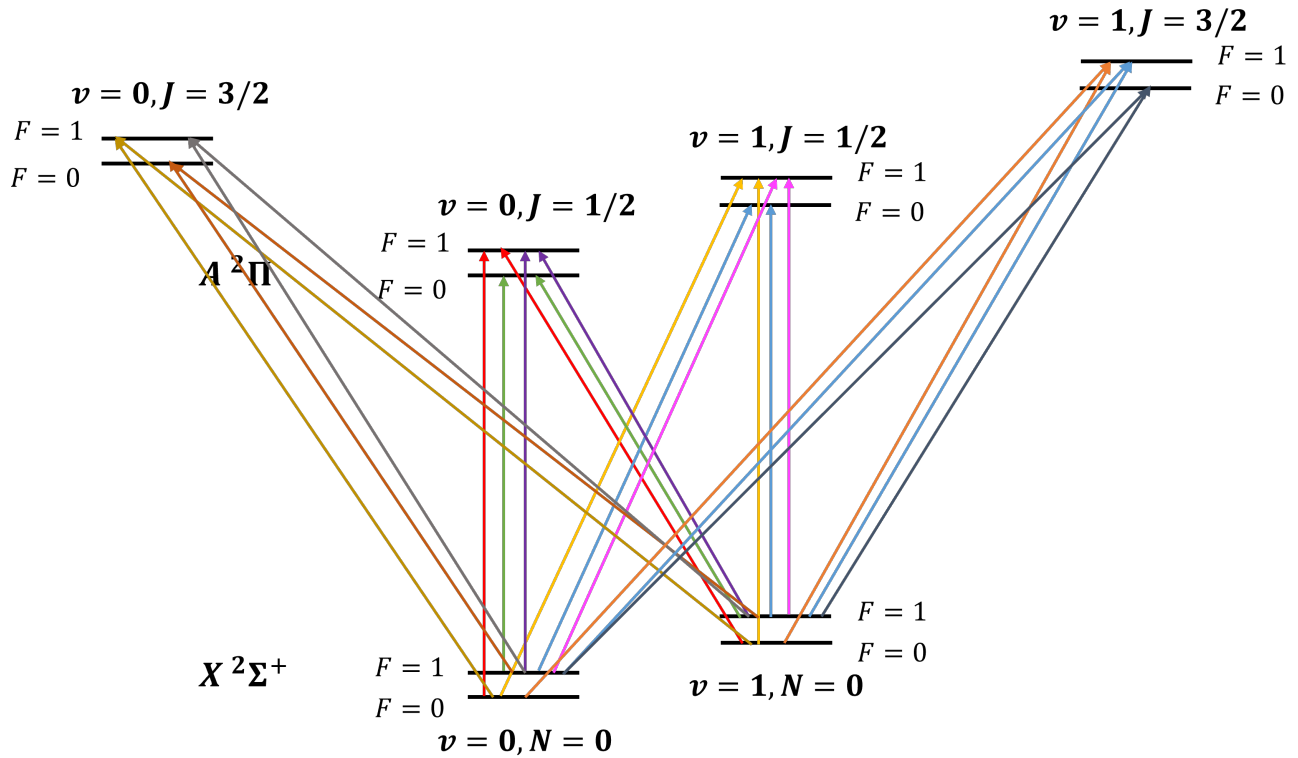
5.1 The Raman transition and the lasers

A Raman system will be built to drive this transition. The system diagram is shown in Fig. 5.1. The Raman system uses the $X\text{ }^2\Sigma^+$ to $A\text{ }^2\Pi$ transition. Two far-detuned lasers with wavelengths of 1064 nm (from Precilaser, 5 kHz linewidth) and 1134 nm (from Toptica, 20 kHz

linewidth) are used to drive these four vibrational transitions shown in Fig. 5.1. The frequency difference of the two lasers is set to the frequency of the CaF $X^2\Sigma^+$ (v, N) = (0, 1) $\rightarrow$ (1, 0) transition. Each $N = 0$ state of the ground electronic state or $J = 1/2$ state on the first excited electronic state has two hyperfine components $F = 0$ and $F = 1$. Some hyperfine transitions can be driven between these rotational levels, all of which are useful for the clock.



(a) Raman transitions driven by lasers



(b) Raman hyperfine components

Figure 5.1: Raman system for driving the CaF clock transition.

The Rabi frequency characterizes the coupling between the molecules and the light. It is an

important parameter for controlling the lasers in experiment. For a three-level system, the expression for the Rabi frequency is derived from the two-level system. The expression for the Rabi frequency in a two-level system is:

$$\Omega = -\frac{\langle g|\hat{\epsilon} \cdot \vec{d}|e\rangle E_0}{\hbar} \quad (5.1)$$

where g and e are the lower and upper states, $\hat{\epsilon}$ indicates the polarization of the laser field and d is the molecular dipole operator. E_0 is the amplitude of the electric field.

Since we choose a very large detuning the excited state population is always very small and then the four-level Raman system can be considered as an effective two-level system [58]. The effective Raman Rabi frequency can be written as:

$$\Omega_R = \sum_{n=1,2} \frac{\Omega_{1n}\Omega_{2n}}{2\Delta_n} \quad (5.2)$$

where n represents different vibrational states of the excited electronic state; Ω_{1n} and Ω_{2n} are Rabi frequencies between different vibrational states of $X^2\Sigma^+$ and $A^2\Pi$ electronic states; Δ_n is the average of detunings of transitions from two vibrational states of the $X^2\Sigma^+$ state to one vibrational state of $A^2\Pi$ state:

$$\Delta_n = \frac{\Delta_1 + \Delta_2}{2} \quad (5.3)$$

where the subscripts 1 and 2 represent different vibrational states of the ground electronic state.

Because the 1064 nm laser has a high power at the 50 W level, the Raman Rabi frequency of this system can reach MHz level, which is big enough to drive this Raman transition. Fig. 5.2 shows the calculated Raman Rabi frequency of the laser system with different laser powers: the power of the 1064 nm laser is fixed to 50 W in this calculation, the waist of the laser beam in the calculation is $w = 10 \mu\text{m}$. The transition dipole moment of the $X - A$ transition of CaF is 5.95 D, the detunings are $\Delta_1 = 1.334 \times 10^{15}$ rad/s and $\Delta_2 = 1.390 \times 10^{15}$ rad/s. The Franck-Condon factors are presented in Tab. 5.1. The calculation shows that the Raman Rabi

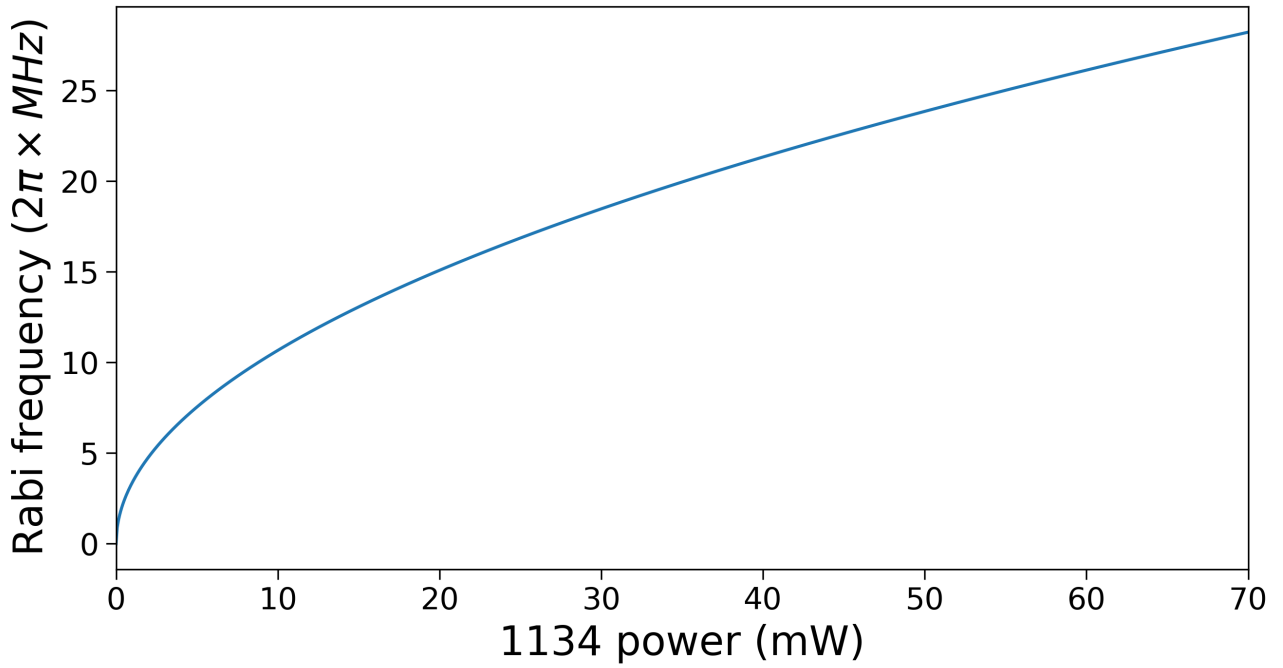


Figure 5.2: Raman Rabi frequency of the CaF vibrational transition vs. the power of the 1134 nm laser.

(v, v')	Franck-Condon factor
(0,0)	0.978
(0,1)	0.0223
(0,2)	1.74×10^{-5}
(1,0)	0.0216
(1,1)	0.935
(1,2)	0.0435
(1,3)	4.58×10^{-5}

Table 5.1: Franck-Condon factors used in the Raman Rabi frequency calculation. From [1]

frequency of the target transition is at the 10 MHz level depending on the choice of laser power (0-70 mW for the 1134 nm laser, 50 W for the 1064 nm laser).

These two lasers are locked to an ultra-stable optical cavity with finesse of 3×10^5 using super-polished mirrors and an ultra-low expansion glass spacer inside a vacuum housing. The cavity is thermally stabilized at the temperature where the thermal expansion coefficient crosses zero. The Pound-Drever-Hall (PDH) technique is used to narrow the linewidths of the two lasers to less than 10 Hz. The details of the locking will be introduced next.

5.2 Pound-Drever-Hall lock

5.2.1 Working principle of a PDH lock

The Pound-Drever-Hall (PDH) lock [59] is a technique to stabilize lasers to very low linewidths even below 1 Hz. In a PDH locking setup, the laser is incident on an optical cavity and the laser is modulated to apply sidebands whose frequency spacing is much larger than the cavity linewidth. When the carrier frequency of the laser is near resonance, the sidebands are off-resonant, and the interference between the carrier and the sidebands will generate a beatnote which contains the phase shift between the laser and the cavity. The beatnote is mixed with a local oscillator at the modulation frequency to recover the imaginary part of the reflection coefficient. This signal is very sharp near resonance (see in Fig. 5.3.), so it is a desired discriminator for locking. The mathematical model for PDH is briefly described here [60].

In a Fabry-Perot cavity, the reflection coefficient $F(\omega)$ is the ratio of the electric field of the reflected laser beam ($E_{\text{ref}} = E_1 e^{i\omega t}$) and the incident beam ($E_{\text{inc}} = E_0 e^{i\omega t}$):

$$F(\omega) = \frac{E_{\text{ref}}}{E_{\text{inc}}} = \frac{r(\exp(i\frac{\omega}{\Delta\nu_{\text{fsr}}}) - 1)}{1 - r^2 \exp(i\frac{\omega}{\Delta\nu_{\text{fsr}}})} \quad (5.4)$$

where r is the reflection coefficient of cavity mirrors, $\Delta\nu_{\text{fsr}}$ is the free spectral range of the cavity.

The modulated electric field of the laser beam is:

$$E_{\text{inc}} = E_0 e^{i(\omega t + \beta \sin \Omega t)} \quad (5.5)$$

Expanding the above expression using Bessel functions and treating each beam separately, the reflected electric field is:

$$E_{\text{ref}} = E_0 [F(\omega) J_0(\beta) e^{i\omega t} + F(\omega + \Omega) J_1(\beta) e^{i(\omega + \Omega)t} - F(\omega - \Omega) J_1(\beta) e^{i(\omega - \Omega)t}] \quad (5.6)$$

Then the power of the reflected beam is:

$$P_{\text{ref}} = P_c |F(\omega)|^2 + P_s (|F(\omega + \Omega)|^2 + |F(\omega - \Omega)|^2) \quad (5.7)$$

$$+ 2\sqrt{P_c P_s} (\text{Re}[F(\omega)F^*(\omega + \Omega) - F^*(\omega)F(\omega - \Omega)] \cos \Omega t) \quad (5.8)$$

$$+ \text{Im}[F(\omega)F^*(\omega + \Omega) - F^*(\omega)F(\omega - \Omega)] + (2\Omega \text{ terms}) \quad (5.9)$$

In the above expression, ω is the carrier frequency, Ω is the modulation frequency, and the frequencies of the upper and lower sidebands are $\omega \pm \Omega$. Only the terms including the phase of the reflected carrier can be used as the error signal, so the $F(\omega)F^*(\omega + \Omega) - F^*(\omega)F(\omega - \Omega)$ term will be measured. When the carrier is near resonance and the modulation frequency is much higher than the cavity linewidth, the sidebands can be regarded as totally reflected, $F(\omega \pm \Omega) \approx -1$. Then $F(\omega)F^*(\omega + \Omega) - F^*(\omega)F(\omega - \Omega) \approx -2i\text{Im}[F(\omega)]$ becomes purely imaginary. Then the cosine term in Eq. 5.9 disappears, so the error signal is written only using the imaginary term as:

$$\epsilon = -2\sqrt{P_c P_s} \text{Im}[F(\omega)F^*(\omega + \Omega) - F^*(\omega)F(\omega - \Omega)] \quad (5.10)$$

The shape of this error signal is shown in Fig. 5.3: the x axis shows the frequency of the scanning laser. The y axis shows the imaginary part of the expression $F(\omega)F^*(\omega + \Omega) - F^*(\omega)F(\omega - \Omega)$. In this figure, $r = 0.999$, $\omega/\Delta f_{\text{fsr}}$ is between -1 and 1, $\Omega/\Delta f_{\text{fsr}}$ is set to 100.

A simplified PDH setup for one laser in our experiment is shown in Fig. 5.4.

The lasers in our experiment (1064 and 1134 nm) are both coupled to an ultra-stable cavity from opposite directions. Fig. 5.4 just shows one side of the experiment to demonstrate the working principle of PDH lock. Both lasers used in our experiment have fibre output. The laser beam first passes through an isolator to prevent back reflection, then the combination of a $\lambda/2$ waveplate and a polarizing beam splitter (PBS) to split the beam to the experiment and the locking system. The electro-optical modulator (EOM) driven by a function generator adds 9 MHz sidebands by frequency modulation to the laser light required for PDH lock. This function generator also outputs a reference signal to the proportional-integral-derivative (PID)

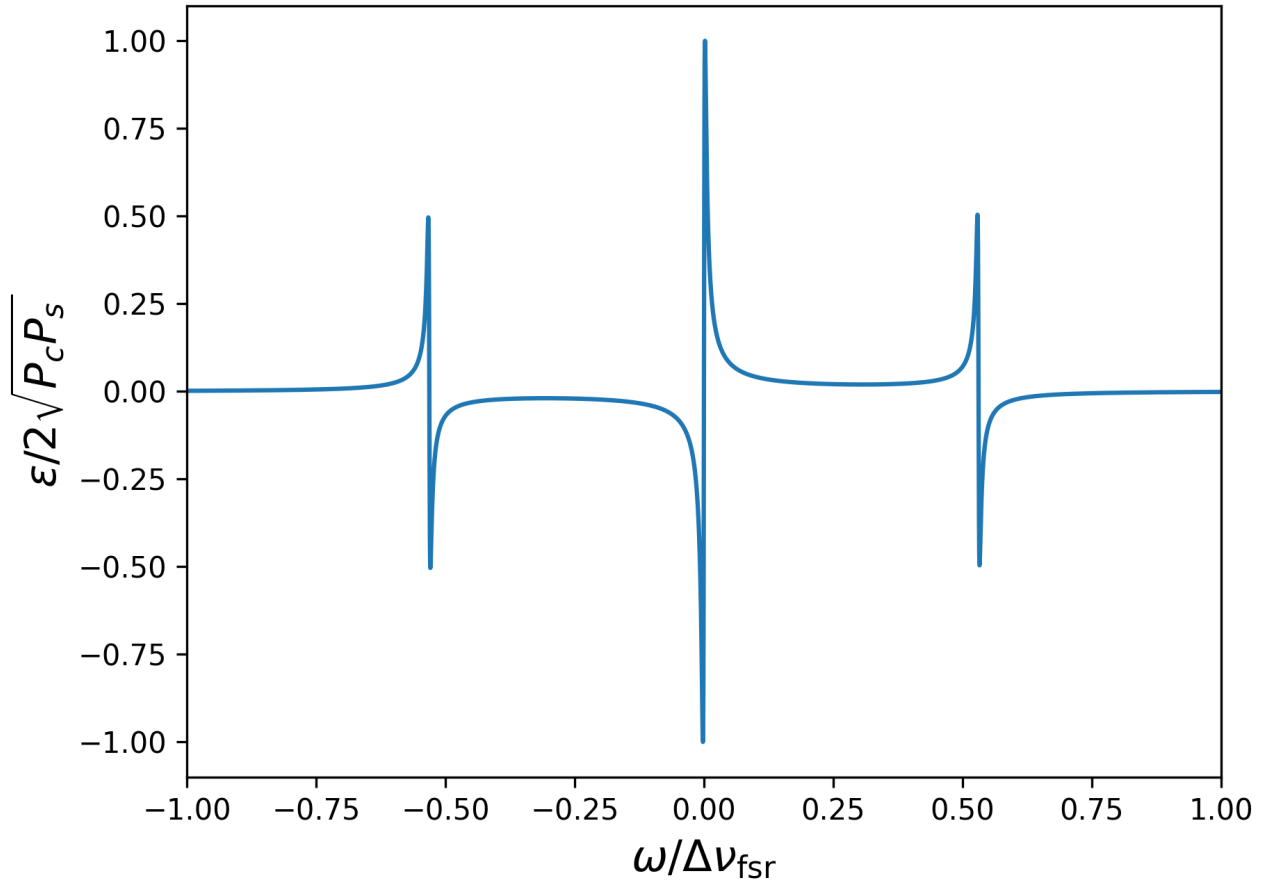


Figure 5.3: A typical Pound-Drever-Hall signal (from calculation).

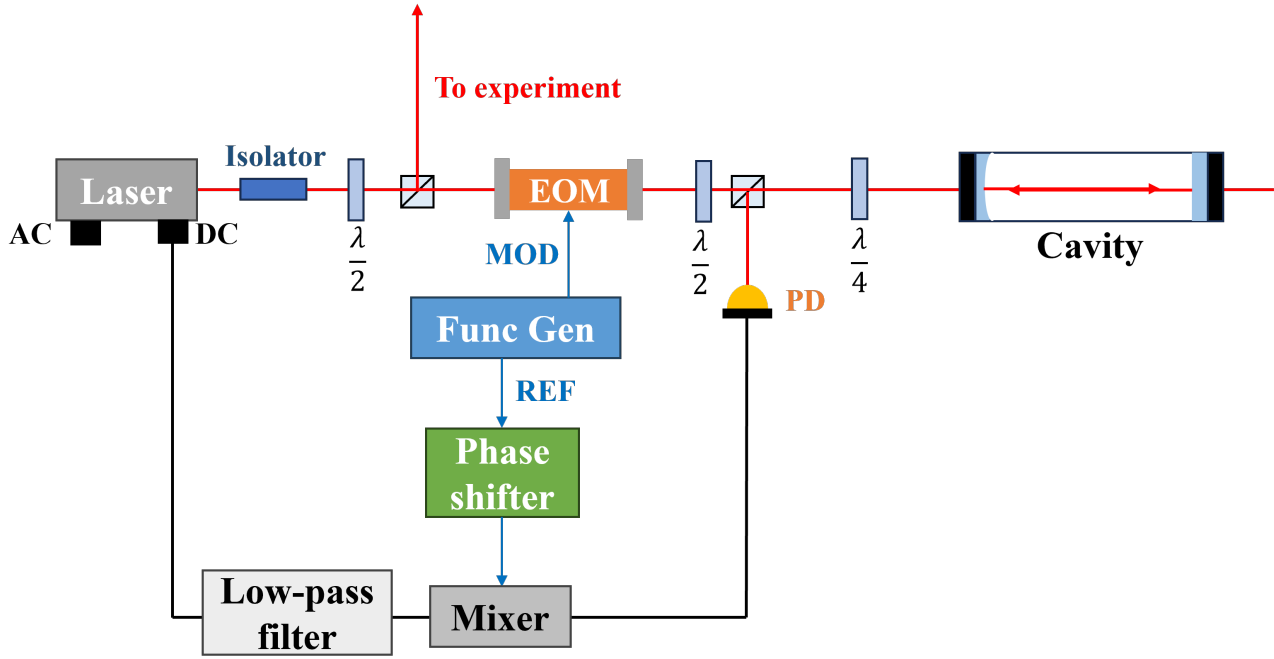


Figure 5.4: The simplified PDH lock setup for the 1134 nm laser in our experiment.

controller. The modulated light passes through a combination of a $\lambda/2$ waveplate and a PBS again then to the cavity. The reflected beam from the cavity will reflect on the same PBS controlled by the $\lambda/4$ beamsplitter. This beam of the reflected cavity signal is detected by a photodiode (PD) for feedback to the laser. The feedback process is done by a P^3I^2D controller to the laser DC input which can receive a wide range of control frequency.

5.2.2 Experimental setup

Fig. 5.5 shows the experimental setup for PDH lock of the 1064 and 1134 nm lasers, which are used for building the CaF Raman system. The 1134 nm laser is a Toptica DL pro. A FALC pro with PI^3D^2 feedback is used for the PDH locking. The 1064 nm laser is from Precilaser, and a Koheron PI200 is used for the PDH locking. The isolators are used to prevent the back reflections of the laser beams. The $\lambda/4$ and $\lambda/2$ waveplates are used for controlling the laser beam polarizations. The 9 MHz sidebands for PDH locking are generated using function generators and fibre EOMs for both lasers. The optical paths of the two lasers overlap and are well aligned to the ultra stable cavity. The laser beams with different frequencies are separated by gratings and detected using different photodiodes. The cavity in the figure is an ultra-stable

cavity which is used to generate the PDH signal.

5.2.3 Alignment of the PDH setup

Aligning infrared lasers through a high finesse cavity is hard, the collimation also needs to be well controlled. The steps of the alignment are presented below:

- Measuring the laser beam profile with a CCD camera, then using this information to calculate the best positions to put two lenses which are used to collimate the laser into the cavity: the waist of the laser is on the flat mirror (the right mirror of the cavity in Fig. 5.4) and it matches the mode of the cavity, because the two mirrors of the cavity are plano-plano and plano-concave.
- Shining the collimated laser beam into the cavity, scanning the laser with the frequency range of $1/10$ of the cavity free spectral range, and the scanning speed is chosen to be around 10 - 100 Hz.
- Using a CCD camera to observe the laser beam from the other side of the cavity. When tuning the center frequency of the laser, some high order modes can appear. Then optimizing the alignment until the observed mode looks more like Laguerre-Gauss shape (round) not Hermite-Gauss shape (square), which means the laser beam is more perpendicular to the cavity mirror.
- Tuning the laser frequency to find the lowest mode which can be observed. Repeat the optimization in step 3 until the 00 mode is found, the output power and collimation of the laser beam is better at low modes and optimized at the 00 mode.
- The alignment can be further optimized when the laser is locked, by just maximizing the output power after the cavity received on a photodiode.

The observed laser modes through the cavity are shown in Fig. 5.6. When the laser is well aligned, the 00 mode should be much stronger than other modes, only one round peak can be observed at the resonant frequencies.

5.2.4 PDH locking result

1134 nm laser

For the 1134 nm laser, a Toptica FALC pro is used for locking. There are several PID parameters that can be tuned in the software TOPAS DLC pro from Toptica. The power spectrum density of the reflected beam from the cavity is shown in Fig. 5.7: the servo bumps appear at 0.5 MHz. The best PID parameters of the FALC pro are set to: P Gain = -25 dB, I1 = 15 kHz, I2 = 25 Hz, D1 = 40 kHz, D2 = 420 kHz. The quality of the lock can be observed from the power spectrum density (PSD) and the transmission signal. The shape of servo bumps (see Fig. 5.8) at the side of the centre frequency on the PSD reflect the stability of the lock. Empirically, when the servo bumps appear at ± 1 to 5 MHz, and the signal power around centre frequency (0 MHz) is very low (close to zero on the PSD), the locking stability would be really good. The stability of the lock increases when the separation of the servo bumps increases, but too high frequency means the locking is oscillating, which can be observed on the transmission signal. The signal power around the centre frequency is not low enough, which means there are some low frequency noise remain, so the PDH lock for the 1134 nm laser currently only remains locked for about 30 minutes.

1064 nm laser

For the 1064 nm laser, a Koheron PI200 is used for locking. The different PI parameters are tuned by the settings on the PI200. Fig. 5.8 shows the power spectral density of the reflected 1064 nm beam from the cavity. The locking stability of this laser is really good, the laser can stay locked for even several days.

Laser frequency and stability measurement

The frequencies and stabilities of the two Raman lasers are measured using an optical frequency comb (OFC) from the company menlo. Fibre links are built between our CCM lab (basement)

and the AION lab (ground), the two lasers are sent upstairs and beat with the OFC in the AION lab. Our clock lasers are compared with a reference laser at 698 nm in the AION lab to get the absolute frequency and stability (see Fig. 5.9). The linewidth of the 1134 nm and 1064 nm lasers are measured to be 2.6 Hz and 1.5 Hz, which is good enough for the clock experiment, the result is shown in Fig. 5.9. In this figure, the x axis is the averaging time of making the beat note between the laser and OFC, the y axis is the Allan deviation which reflects the relative frequency uncertainty between the laser and OFC. The minimum Allan deviation dropped to minimum at 100 and 20 s for the 1134 and 1064 nm lasers, because the increase of averaging time can make some short term oscillation averaged out, the Allan deviation will reach a minimum at certain averaging time, this time depends on the properties of the oscillator system (e.g. the laser noise level at different frequencies). When the averaging time is above this threshold, the long term drift of the laser frequency will dominate and make the Allan deviation increase.

5.3 Summary

In this Chapter, the design of the clock experiment is presented. The lasers and transitions used for making the Raman clock system are introduced. An important technique used to stabilize the Raman lasers: PDH locking, is introduced theoretically, and the block diagram of the experimental setup in our lab is also presented. The two Raman lasers have been implemented in the lab and locked to a good stability. With the prepared Raman laser system, the CaF clock transition can be driven when the MOT and the lattice are well prepared.

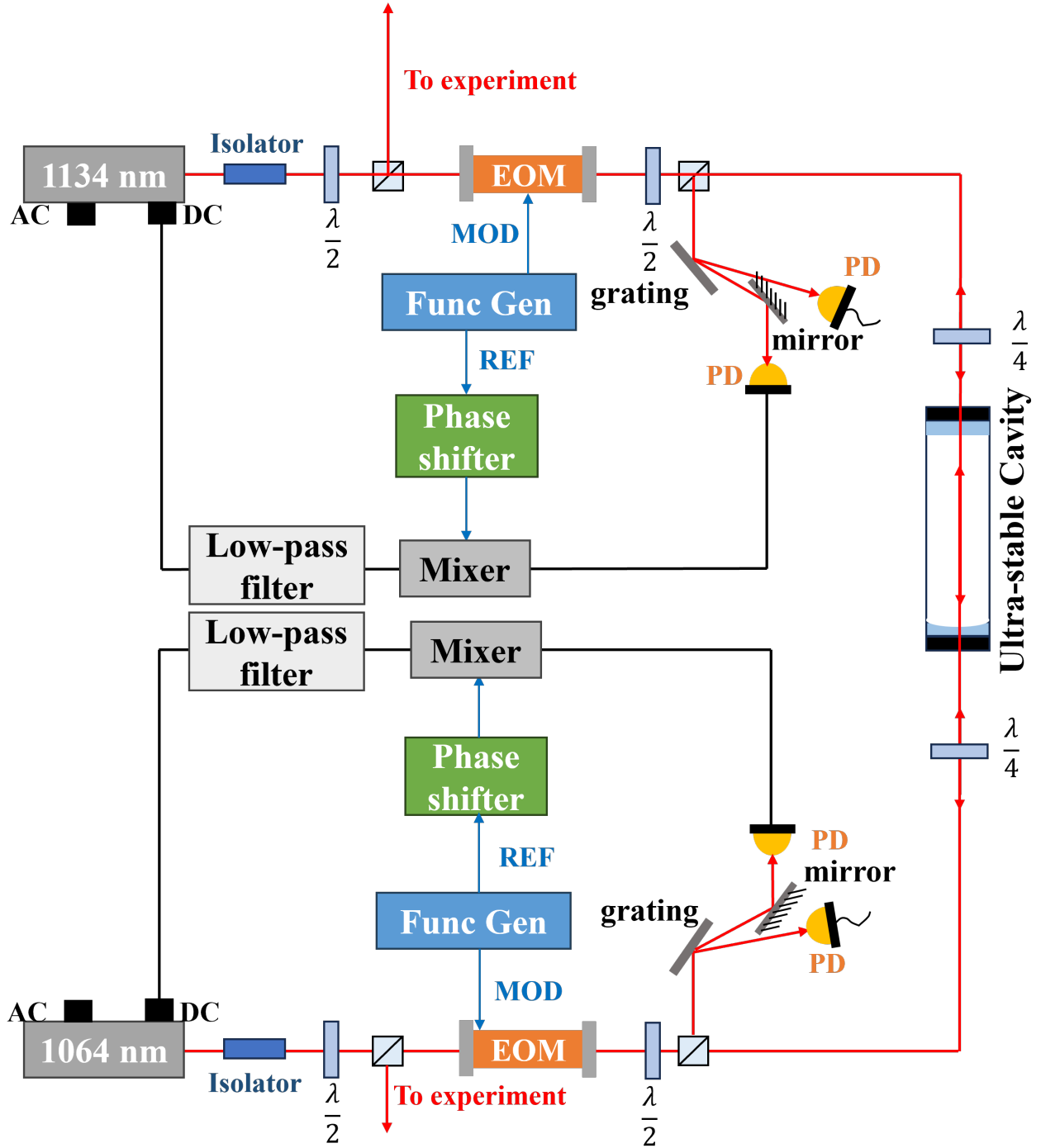


Figure 5.5: The PDH lock setup in our experiment.

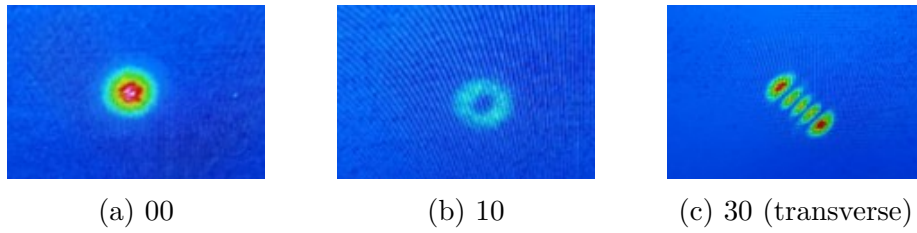


Figure 5.6: Observed transverse laser modes after the ultra-stable cavity.

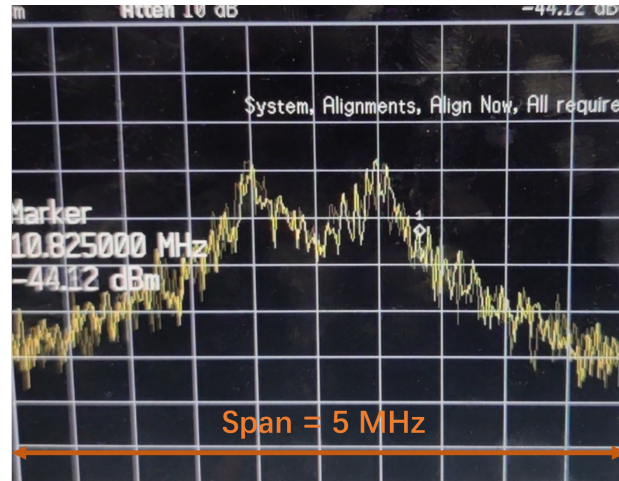


Figure 5.7: Measured power spectrum density of the reflected 1134 nm beam from the ultra-stable cavity.

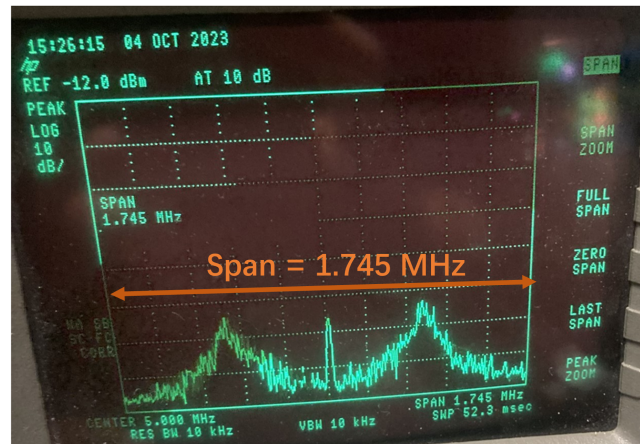


Figure 5.8: Measured power spectrum density of the reflected 1064 nm beam from the ultra-stable cavity.

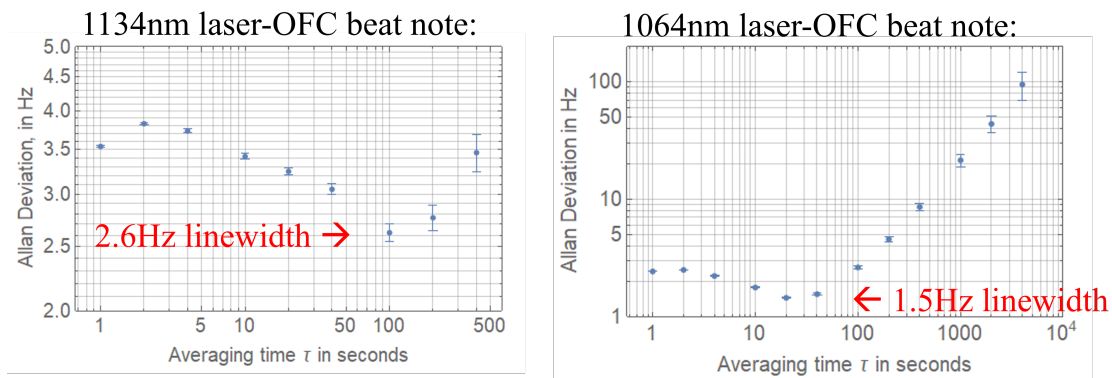


Figure 5.9: The frequency stability of the 1064 nm and 1134 nm laser beating with an optical frequency comb. These results are measured by Jonas Rodewald.

Chapter 6

Evaluating the potential accuracy of a CaF lattice clock

In this chapter, the accuracy of the CaF clock is estimated. Several sources of systematic uncertainties are discussed, and the total estimated uncertainty of the clock is calculated.

6.1 Optical lattice

Optical lattices [61] are created by a set of gaussian laser beams with identical frequencies, but their polarizations, directions of propagation, amplitudes and phases can be different. A general expression of the total optical electric field at position $\vec{r}$ can be written as:

$$\mathbf{E}_{tot}(\vec{r}) = \frac{1}{2} \sum_j E_{0j} \vec{\epsilon}_j e^{i(\mathbf{k}_j \cdot \vec{r} - \omega_L t + \phi_j)} + c.c. \quad (6.1)$$

E_{0j} , $\vec{\epsilon}_j$, $\vec{k}_j$ and ϕ_j are the amplitude, polarization, wavevector and phase offset of laser beam j , and ω_L is their common frequency.

The total intensity can be expressed as:

$$I_{tot} = \frac{1}{2} c \epsilon_0 |\mathbf{E}_{tot}|^2 \quad (6.2)$$

Considering the interaction of the laser field and diatomic molecules, the interaction Hamiltonian is: $H' = -\mathbf{d} \cdot \mathbf{E}_{tot}$, where $\mathbf{d}$ is the dipole moment operator of the molecule. Using the second order perturbation theory, the energy shift of a nondegenerate level i can be expressed as:

$$\Delta W_i = -\frac{1}{4}E_0^2 \sum_{j \neq i} \left(\frac{\langle i | \mathbf{d} \cdot \boldsymbol{\epsilon}^* | j \rangle \langle j | \mathbf{d} \cdot \boldsymbol{\epsilon} | i \rangle}{\hbar(\omega_{ji} - \omega_L)} + \frac{\langle i | \mathbf{d} \cdot \boldsymbol{\epsilon} | j \rangle \langle j | \mathbf{d} \cdot \boldsymbol{\epsilon}^* | i \rangle}{\hbar(\omega_{ji} + \omega_L)} \right) \quad (6.3)$$

where ω_{ji} is the angular frequency of transition between state j and state i .

Using spherical coordinates, the effective Stark shift operator becomes [46]:

$$H_S = -\frac{E_0^2}{4} \sum_{K=0}^2 \sum_{P=-K}^K (-1)^P \mathcal{A}_P^K \mathcal{P}_{-P}^K \quad (6.4)$$

where E_0 is the total amplitude, $\mathcal{A}_P^K$ are polarizability operators related to polarizabilities and quantum numbers, $\mathcal{P}_P^K$ are polarization tensors calculated from the polarization of the light. The $K = 0$ terms in the matrix elements of H_S are related to the scalar part of the Stark shift, the $K = 1$ terms are related to the vector part, and the $K = 2$ terms are related to the tensor part of the Stark shift. Taking suitable parameters into this Stark shift operator, the potential depth distribution can be calculated. The laser beams are assumed linearly polarized for the convenience of theoretical analysis and experimental control.

Polarizabilities $\alpha = \frac{|\vec{p}|}{||E||}$ are used to describe the ac-Stark shift. The polarizabilities can be calculated from the second-order perturbation theory, and for diatomic molecules, they are expressed as ([46]):

$$\alpha_{\parallel} = \sum_j \left(\frac{1}{\hbar(\omega_j + \omega_L)} + \frac{1}{\hbar(\omega_j - \omega_L)} \right) |\langle X, {}^2\Sigma | d_0 | j, {}^2\Sigma \rangle|^2 \quad (6.5)$$

$$\alpha_{\perp, \Omega} = \sum_k \left(\frac{1}{\hbar(\omega_{k, \Omega} + \omega_L)} + \frac{1}{\hbar(\omega_{k, \Omega} - \omega_L)} \right) |\langle X, {}^2\Sigma | d_1 | j, {}^2\Pi_{\Omega} \rangle|^2 \quad (6.6)$$

$$\alpha_{\perp} = \frac{1}{2}(\alpha_{\perp, \frac{1}{2}} + \alpha_{\perp, \frac{3}{2}}) \quad (6.7)$$

$$\beta_{\perp, \Omega} = \sum_k \left(\frac{1}{\hbar(\omega_{k, \Omega} + \omega_L)} - \frac{1}{\hbar(\omega_{k, \Omega} - \omega_L)} \right) |\langle X, {}^2\Sigma | d_1 | j, {}^2\Pi_{\Omega} \rangle|^2 \quad (6.8)$$

The scalar (α_0), vector (α_1) and tensor (α_2) parts of polarizability are obtained from the above

expressions:

$$\alpha_0 = \frac{1}{3}(\alpha_{\parallel} + 2\alpha_{\perp}) \quad (6.9)$$

$$\alpha_1 = \frac{1}{2}(\beta_{\perp, \frac{1}{2}} - \beta_{\perp, \frac{3}{2}}) \quad (6.10)$$

$$\alpha_2 = \frac{2}{3}(\alpha_{\parallel} - \alpha_{\perp}) \quad (6.11)$$

According to the above expressions, the polarizabilities are calculated from transition frequencies and dipole moments from $X^2\Sigma$ state to other electronic states.

In our experiment, we plan to make a 1D optical lattice using two counter-propagating laser beams. The electric field is expressed as:

$$\mathbf{E}(\mathbf{z}) = E_0 \vec{\epsilon}_0 e^{-i\omega_L t} \cos kz + c.c. \quad (6.12)$$

where ϵ_0 is the polarization direction of the laser beams. The polarization direction of two laser beams can be parallel or perpendicular to each other (see Fig. 6.1). For making a 1D optical lattice, only the parallel case can be chosen because the interference pattern can form optical potential to trap the atoms/molecules. The expression for the intensity distribution, after time-averaging over one cycle, is:

$$I_{parallel} = 2c\epsilon_0 \cos^2(kz) \quad (6.13)$$



Figure 6.1: Two cases of polarization of a 1D lattice: (a) parallel; (b) perpendicular.

6.2 Estimation of systematic uncertainties of the clock

The accuracy of molecular clocks is described by the fractional uncertainty of the transition frequency: $\frac{1}{f_0} \frac{df_0}{dx}$, where f_0 is the clock transition, x is the parameter being studied (the details can be found in [62]). Here I present analysis for several important parameters: lattice frequency, lattice intensity, Zeeman effect, DC Stark shift, blackbody shift and Doppler shift.

6.2.1 Lattice frequency

The uncertainty related to lattice frequency is caused by the Stark shift, which is the energy shift induced by the interaction between the laser field and dipole moment of the molecule. The interaction Hamiltonian is:

$$H' = -\mathbf{d} \cdot \mathbf{E}_{tot} \quad (6.14)$$

The uncertainty related to lattice frequency is expressed as:

$$\frac{1}{f_0} \frac{df_0}{df_L} = -\frac{I}{6hc\epsilon_0 f_0} \Delta \left(\frac{d\alpha_{||}}{df_L} + \frac{d\alpha_{\perp,1/2}}{df_L} + \frac{d\alpha_{\perp,3/2}}{df_L} \right) \quad (6.15)$$

where Δ means the difference of the quantities below between the $v = 0$ and $v = 1$,

$$\frac{d\alpha_{||}}{df_L} = \sum_j \frac{d_j^2}{h} \left(-\frac{1}{(f_j + f_L)^2} + \frac{1}{(f_j - f_L)^2} \right) \quad (6.16)$$

$$\frac{d\alpha_{\perp}}{df_L} = \sum_k \frac{d_k^2}{h} \left(-\frac{1}{(f_k + f_L)^2} + \frac{1}{(f_k - f_L)^2} \right) \quad (6.17)$$

To calculate the frequency shift due to the ac-Stark shift [57], the polarizabilities of both the $v = 0$ and the $v = 1$ states need to be calculated. The data I use to calculate these polarizabilities are given in Tables 6.1, 6.2 and 6.3.

Upper State	Transition Frequency(THz)	Franck-Condon factor
$B^2\Sigma^+, v = 0, N = 0$	564.582695	0.998
$B^2\Sigma^+, v = 1, N = 0$	548	0.00195
$D^2\Sigma^+, v = 0, N = 1$	904.131747	1
$D^2\Sigma^+, v = 1, N = 1$	923	0
$A^2\Pi, \Omega = 0.5, v = 0, J = 0.5$	494.432203	0.978
$A^2\Pi, \Omega = 0.5, v = 1, J = 0.5$	512.073572	0.0223
$A^2\Pi, \Omega = 1.5, v = 0, J = 0.5$	497.432203	0.978
$A^2\Pi, \Omega = 1.5, v = 1, J = 0.5$	515.073572	0.0223
$C^2\Pi, \Omega = 0.5, v = 0, J = 0.5$	905.373209	0.694
$C^2\Pi, \Omega = 0.5, v = 1, J = 0.5$	919.70165	0.258
$C^2\Pi, \Omega = 0.5, v = 2, J = 0.5$	933.892132	0.0441
$C^2\Pi, \Omega = 1.5, v = 0, J = 0.5$	905.373209	0.694
$C^2\Pi, \Omega = 1.5, v = 1, J = 0.5$	919.70165	0.258
$C^2\Pi, \Omega = 1.5, v = 2, J = 0.5$	933.892132	0.0441

Table 6.1: CaF transitions from $X^2\Sigma^+, v = 0, N = 1$. Transition frequencies and Franck-Condon factors are from [1].

Figure 6.2 shows the result of this calculation using Eq. 6.15, Eq. 6.16 and Eq. 6.17. It plots the difference in polarizability between the $v = 0$ and $v = 1$ states as a function of the lattice wavelength. The wavelengths where the polarizability difference is zero are called 'magic wavelengths', except for those transition frequencies. There are three 'magic wavelengths' in the 500 to 700 nm region: 549.5 nm, 599.1 nm and 694.5 nm. At these wavelengths shown in Fig. 6.2, the ac-Stark shift of the clock transition, due to the presence of the lattice, is zero. A lattice with its frequency at 694.5 nm would be desirable, because the polarizability changes slowly around this wavelength, which means the systematic frequency uncertainty due to the ac-Stark shift can be suppressed to minimum.

Fig 6.3 shows the relation between uncertainty (described in Eq. 6.15) and lattice wavelength. A good lattice frequency should be chosen from the zero crossing frequencies (except for those transition frequencies) in Fig. 6.3, or close to these frequencies to suppress the systematic

Upper State	Transition Frequency (THz)	Franck-Condon factor
$B^2\Sigma^+, v=0, N=0$	547.109507	0.00192
$B^2\Sigma^+, v=1, N=0$	564.5	0.993
$B^2\Sigma^+, v=2, N=0$	581.3	0.00457
$D^2\Sigma^+, v=1, N=1$	906.201015	1
$D^2\Sigma^+, v=0, N=1$	886.658559	0
$A^2\Pi, \Omega=0.5, v=0, J=0.5$	476.959015	0.0216
$A^2\Pi, \Omega=0.5, v=1, J=0.5$	494.600384	0.935
$A^2\Pi, \Omega=0.5, v=2, J=0.5$	511.6	0.0435
$A^2\Pi, \Omega=1.5, v=0, J=0.5$	479.959015	0.978
$A^2\Pi, \Omega=1.5, v=1, J=0.5$	497.600384	0.0223
$A^2\Pi, \Omega=0.5, v=2, J=0.5$	514.6	0.0435
$C^2\Pi, \Omega=0.5, v=0, J=0.5$	887.900021	0.249
$C^2\Pi, \Omega=0.5, v=1, J=0.5$	902.228462	0.282
$C^2\Pi, \Omega=0.5, v=2, J=0.5$	916.418944	0.35
$C^2\Pi, \Omega=1.5, v=0, J=0.5$	887.900021	0.249
$C^2\Pi, \Omega=1.5, v=1, J=0.5$	902.228462	0.282
$C^2\Pi, \Omega=1.5, v=2, J=0.5$	916.418944	0.35

Table 6.2: Transitions from $X^2\Sigma^+, v=1, N=1$. Transition frequencies are from [2] and [1].

Transitions	Transition Dipole Moments (D)
$X^2\Sigma^+ - A^2\Pi$	5.95
$X^2\Sigma^+ - B^2\Sigma^+$	4.70
$X^2\Sigma^+ - C^2\Pi$	1.30
$X^2\Sigma^+ - D^2\Sigma^+$	0.79

Table 6.3: Transition dipole moments from [1].

uncertainty from the lattice frequency. In the first step of the clock experiment, one of the Raman laser at 1064 nm is chosen as the lattice laser. 1064 nm is not one of the 'magic wavelengths', but the systematic frequency uncertainty of the clock from lattice frequency at 1064 nm is small, it is calculated to be 3.70×10^{-20} . In the future, maybe we will implement a lattice laser, with its frequency at the 'magic wavelength' 694.5 nm, then this source of uncertainty can be eliminated.

6.2.2 Lattice intensity

The uncertainty related to the lattice intensity is expressed as:

$$\frac{1}{f_0} \frac{df_0}{dI_L} \quad (6.18)$$

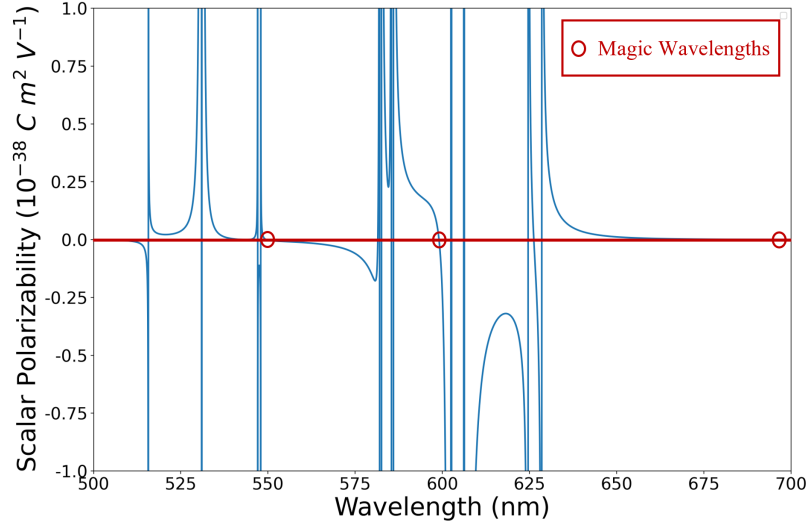


Figure 6.2: Scalar polarizability between $v = 0$ and $v = 1$ states, calculated using expressions from Sec. 6.1. The 'magic wavelengths' are: 549.5 nm, 599.1 nm and 694.5 nm.

where

$$\frac{df_0}{dI_L} = \frac{d\Delta f}{dI_L} = \frac{d}{dI_L} \left(-\frac{I_l}{2hc\epsilon_0} \Delta\alpha \right) = -\frac{\Delta\alpha}{2hc\epsilon_0}$$

so

$$\frac{1}{f_0} \frac{df_0}{dI_L} = -\frac{\Delta\alpha}{2hc\epsilon_0 f_0} \quad (6.19)$$

From the above expression, the uncertainty related to the lattice intensity (described in Eq. 6.19, see Fig 6.4) is proportional to the difference of polarizabilities on upper and lower states, and it is independent of the lattice intensity. So, we can reduce this source of uncertainty by selecting an appropriate lattice wavelength where the difference of polarizabilities is zero or small enough to be neglected. These are the magic wavelengths discussed above and illustrated in Fig. 6.2.

6.2.3 Hyperfine splittings and Zeeman effect

There are several hyperfine splittings in a vibrational transition. Each hyperfine level can split into several sub-levels in magnetic fields, namely the Zeeman effect. In this section, the frequency shift of the clock due to the hyperfine splittings and the Zeeman effect is discussed.

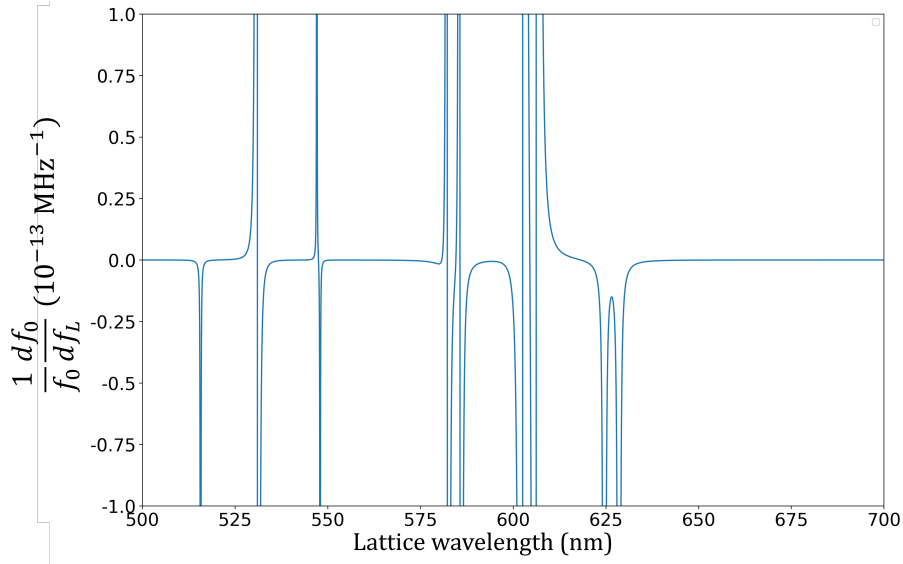


Figure 6.3: Calculated uncertainty using Eq. 6.16 and Eq. 6.17 related to the lattice frequency.

To evaluate the shifts due to the hyperfine structure and Zeeman effect, I use the basis $|\Lambda, N, S, J, I, F, m_F\rangle$ to calculate different matrix elements. The expression of the Hamiltonian of the hyperfine structure is ([63]):

$$H_{hfs} = b\mathbf{I} \cdot \mathbf{S} + cI_z S_z + C_I \mathbf{I} \cdot \mathbf{N} \quad (6.20)$$

which transforms to [46]:

$$H_{hfs} = (b + \frac{c}{3})\mathbf{I} \cdot \mathbf{S} + \frac{\sqrt{6}}{3}cT_{p=0}^2(\mathbf{I}, \mathbf{S}) + C_I \mathbf{I} \cdot \mathbf{N} \quad (6.21)$$

$$= (b + \frac{c}{3})\mathbf{I} \cdot \mathbf{S} + \frac{\sqrt{6}}{3}cT^2(\mathbf{C}) \cdot T^2(\mathbf{I}, \mathbf{S}) + C_I \mathbf{I} \cdot \mathbf{N} \quad (6.22)$$

$$= (b + \frac{c}{3})\mathbf{I} \cdot \mathbf{S} - \frac{\sqrt{10}}{3}cT^1(\mathbf{I}) \cdot T^1(\mathbf{S}, \mathbf{C}^2) + C_I \mathbf{I} \cdot \mathbf{N} \quad (6.23)$$

where $T_p^k(\mathbf{T})$ is a spherical tensor for describing the couplings between quantum numbers:

$$T_p^k(\mathbf{T}) = \sum_{p'}^k T_{p'}^k(\mathbf{T}) \mathcal{D}_{p'p}^{(k)}(\omega) \quad (6.24)$$

The tensor of rank K $T_P^K(\mathbf{R}^{k_1}, \mathbf{S}^{k_2})$ is the combination of two spherical tensors $\mathbf{R}^{k_1}$ and $\mathbf{S}^{k_2}$.

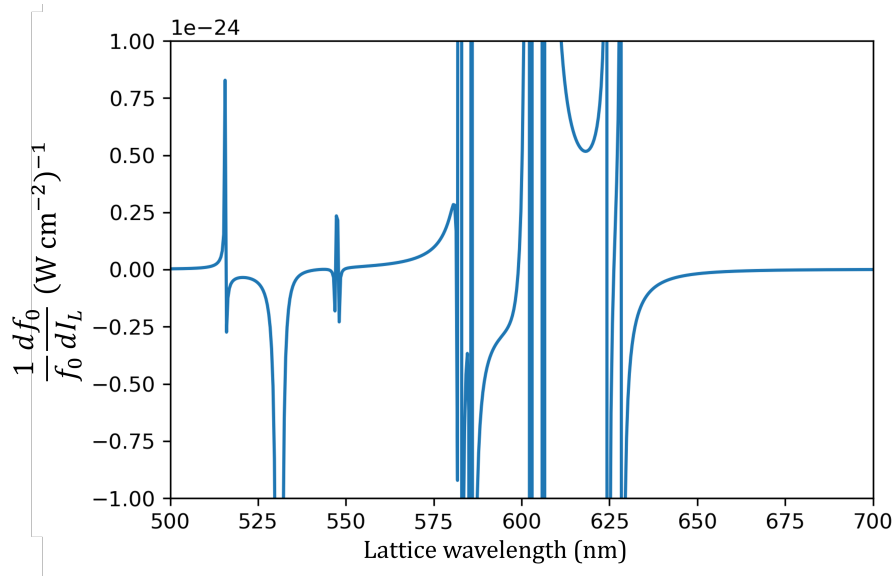


Figure 6.4: Uncertainty related to the lattice intensity, calculated using 6.19.

Taking all possible values from $(K_1 + k_2)$ to $k_1 - k_2$, assuming $k_1 \geq k_2$:

$$T_P^K(\mathbf{R}^{k_1}, \mathbf{S}^{k_2}) = \sum_{p_1 p_2} \langle k_1, k_2, p_1, p_2 | K, P \rangle T_{p_1}^{k_1}(\mathbf{R}) T_{p_2}^{k_2}(\mathbf{S}) \quad (6.25)$$

In spherical tensor algebra, the scalar product is defined as:

$$T^k(\mathbf{R}) \cdot T^k(\mathbf{S}) = \sum_p (-1)^p T_p^k(\mathbf{R}) T_{-p}^k(\mathbf{S}) \quad (6.26)$$

The Hamiltonian describing the Zeeman effect of diatomic molecules in Σ states consists of several parts [46]: the electron spin ($g_S \mu_B B_z T_0^1(\mathbf{S})$), the rotational motion ($-g_r \mu_B B_z T_0^1(\mathbf{N})$), the nuclear spin interaction ($-g_N \mu_N B_z T_0^1(\mathbf{I})$) and the anisotropic correction to the electron spin interaction ($g_l \mu_B B_z \sum_{q=\pm 1}' \mathcal{D}_{0q}^1(\omega)^* T_q^1(\mathbf{S})$):

$$H_Z = g_S \mu_B B_z T_0^1(\mathbf{S}) - g_r \mu_B B_z T_0^1(\mathbf{N}) - g_N \mu_N B_z T_0^1(\mathbf{I}) + g_l \mu_B B_z \sum_{q=\pm 1}' \mathcal{D}_{0q}^1(\omega)^* T_q^1(\mathbf{S}) \quad (6.27)$$

The total shift caused by hyperfine splitting and Zeeman effect is described by the Hamiltonian:

$$H_{tot} = H_{hfs} + H_Z \quad (6.28)$$

Calculating the matrix elements of $\langle \Lambda, N, S, J, I, F, m_F | H_{tot} | \Lambda, N, S, J', I, F', m'_F \rangle$ and diagonalizing them, taking the coefficients from [63], the total energy shifts of each hyperfine level can be evaluated. The result of this calculation is shown in Fig. 6.5 which shows the splittings of different vibrational and rotational states: the vertical axis is the Energy shifted in MHz, the horizontal axis is the strength of magnetic field in Gauss.

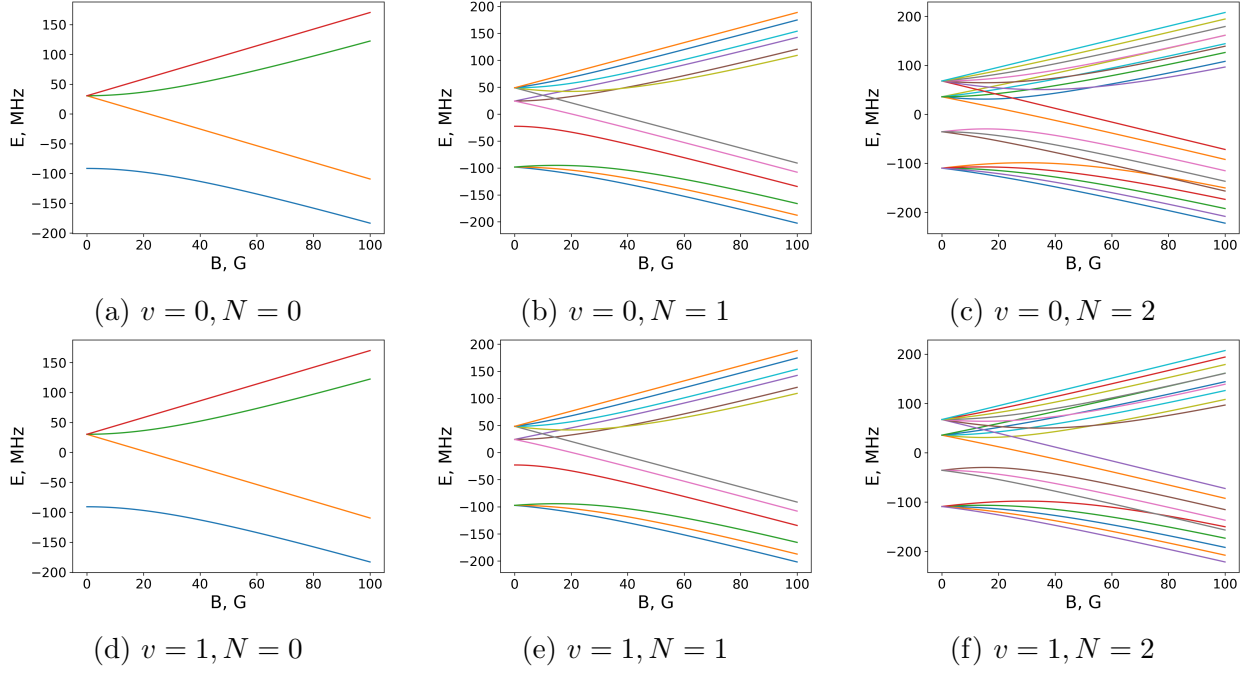


Figure 6.5: Hyperfine and Zeeman splitting on the $X^2\Sigma^+$ state of the CaF molecule.

The $m = \pm 1$ components of the clock transition have equal and opposite linear Zeeman shifts. Using the calculated vibrational dependence of the g-factors [64], we find shifts of $\pm 0.05 \text{ Hz } \mu\text{T}^{-1}$. By controlling the magnetic field to $0.1 \mu\text{T}$ and ensuring that both components are driven equally to within 1%, the fractional uncertainty in the clock frequency from the Zeeman shift is reduced to 3×10^{-18} . The transition with $m = 0$ has a quadratic Zeeman shift. Using the measured vibrational dependence of the hyperfine constants [63], we estimate a shift of $\pm 0.014 \text{ Hz } \mu\text{T}^{-2}$. At $0.1 \mu\text{T}$, the fractional uncertainty is 8×10^{-18} . We note that controlling the magnetic field to $0.1 \mu\text{T}$ can be done by measuring the rotational frequency with a good fractional precision of 7×10^{-18} [62].

6.2.4 Doppler shift

The Doppler shift is one of the main sources of frequency uncertainty of a clock, and it is the reason why we need to cool molecules to ultracold temperatures. The Doppler shift of the clock transition frequency is described as:

$$\frac{\delta f}{f} = \frac{f - f_0}{f_0} = \frac{\langle v_{\parallel} \rangle}{c} - \frac{\langle v^2 \rangle}{2c^2} + \frac{\langle v_{\parallel}^2 \rangle}{c^2} + O(v/c)^3 \quad (6.29)$$

where v is the velocity of molecules, $v_{\parallel}$ is the velocity of molecules along the laser beam. The first term describes the first-order Doppler shift, the second and third term describe the second-order Doppler shift, $O(v/c)^3$ includes high order (higher than 3) terms of velocity. In an optical lattice, the molecules are trapped, so $\langle v_{\parallel} \rangle$ is zero, so the first-order Doppler shift is cancelled.

The second term in Eq 6.29 can be calculated by Maxwell-Boltzmann distribution:

$$\frac{\langle v^2 \rangle}{2c^2} = \frac{3kT}{2mc^2} \quad (6.30)$$

When the CaF molecules are cooled to 5 μ K, the second order Doppler shift becomes 4×10^{-21} .

6.2.5 Systematic uncertainty

Following the discussion and results in the previous subsections, the desired overall systematic uncertainty of the CaF clock can be estimated. According to the discussion in Sec. 6.1, the frequency of the lattice laser is best to be chosen around 694.5 nm. Except for the uncertainties discussed above, the DC Stark shift can be estimated using the vibrational dependence of both the dipole moment and the rotational constant, it is 1.2 Hz (V/cm) $^{-2}$ for the clock transition. From calculation, a 10 mV cm $^{-1}$ uncertainty in the stray field translates to a fractional uncertainty of 7×10^{-18} [62]. When one of the Raman lasers is also used as the lattice laser at 696 nm (close to the 'magic wavelength'), another laser is chosen to be 725 nm. The AC Stark shift produced by the 725 nm laser is negligible, which contributes a fractional shift in clock transition frequency of 9×10^{-22} . All these sources of uncertainties are listed in

Effect	Conditions	Fractional uncertainty
Lattice frequency	$\delta f_{\text{latt}} < 1 \text{ MHz}$	5×10^{-19}
Zeeman shift	$B < 0.1 \mu T$, asymmetry $< 1\%$	7×10^{-18}
DC Stark shift	$E < 10 \text{ mV cm}^{-1}$	7×10^{-18}
Blackbody shift	$\delta T < 250 \text{ mK}$ at 300 K	10^{-18}
Doppler shift	$T = 5 \mu K$	4×10^{-21}
Raman laser	696 nm & 725 nm	$< 9 \times 10^{-22}$

Table 6.4: Projected systematic uncertainties for a CaF clock using a 696 nm lattice. From [3].

Tab. 6.4, they give an overall systematic uncertainty of 1×10^{-17} in the CaF clock transition, the main sources of uncertainty are the Zeeman shift and the DC Stark shift.

Chapter 7

Conclusion

7.1 Summary

This thesis presents the current progress towards making a molecular clock based on the fundamental vibrational transition of CaF.

In Chapter 1, the theory of testing the variation of fundamental constants is briefly introduced, including the theories of fundamental constants and different types of clocks. The QSNET project, which is a collaboration between theoretical and experimental physicists from research communities in the UK, is introduced in this chapter. In this project, we proposed a clock based on the fundamental vibrational transition of CaF, with a natural linewidth of 0.7 Hz.

The theories of molecular spectroscopy of CaF and N₂O are briefly reviewed in Chapter 2, including the electronic, vibrational and rotational spectroscopy for diatomic molecules and triatomic molecules. The level structures of the two molecules (N₂O and CaF) used in our experiment are also presented.

The N₂O spectroscopy experiment is presented in Chapter 3. A list of 165 N₂O lines around 17 μ m is provided with detailed analysis of the frequencies, relative intensities and discussion of uncertainties. The average overall uncertainty for these lines is around 3 MHz, which is limited by the calibration lines from Maki et al. [26]. Our new N₂O linelist provides rich information

of frequencies around $17\ \mu\text{m}$, because most of the lines have never been measured before. With the CaF clock measurements in the future, the accuracy of N_2O linelist can be improved a lot, the frequency uncertainties of the lines will be at least on the 100 kHz level, since we will not rely on the calibration line from previous literature of N_2O anymore. The newly calibrated lines can be used as frequency standards in the $17\ \mu\text{m}$ region.

Using the N_2O spectroscopy, the frequency of the $17\ \mu\text{m}$ laser is calibrated. The measured N_2O lines can be used to search for the fundamental vibrational transition of CaF, the experiment is presented in Chapter 4. Laser cooling theories and experimental setup are first summarized in this chapter. Using the laser cooling setup, with the frequency information of the laser from N_2O spectroscopy, the CaF $(v, N, v', N') = (0, 1, 1, 0)$ vibrational transition is successfully driven for the first time. Four hyperfine transitions are observed with the linewidth of 5-10 MHz. This experiment provides important frequency information for driving the CaF clock transition using the Raman setup.

The Raman system for driving the CaF clock transition is presented in Chapter 5. The theoretical background and states involved in the Raman system are introduced first. Then the working principle and experimental setup of PDH locking is presented. Some methods for aligning the infrared lasers into the ultra-stable cavity are introduced. With this setup, the two Raman lasers (at 1064 nm and 1134 nm) are locked to Hz level linewidth. This linewidth is measured by comparing the frequencies of the lasers in our lab and another 698 nm laser for the Sr clock experiment, and the comparison is done using an optical frequency comb.

When both the Raman and optical lattice experimental setups are ready, the potential accuracy of our proposed CaF clock needs to be evaluated. In Chapter 6, polarizability calculations for molecules in a lattice are presented, and several different sources of uncertainties are analyzed separately. They together give an systematic fractional uncertainty at the 10^{-17} level.

7.2 Future plans

In the near future, the experiment which uses the 17 μm laser to drive the CaF vibrational transition will be improved. In the setup presented in this thesis, the laser is drifting and the electronic noise limits the accuracy of the measurement. A new controller with much lower noise has been implemented in the experiment. A switch will also be installed, that can better control the timing of when the laser is shining on the CaF molecules.

Since the Raman laser system is well prepared, the lasers will be used to drive the CaF molecules in the optical lattice soon, which is a crucial step of making the CaF clock. In the current setup, the Raman lasers have frequencies of 1064 nm and 1134 nm, the 1064 nm laser is also used as the lattice laser, this will introduce some systematic frequency uncertainty of the clock due to the lattice frequency. This uncertainty can be eliminated if we use a laser at 696 nm as the lattice laser and one of the Raman laser, then another Raman laser should be at 725 nm, because the frequency difference between the two lasers should be exactly the frequency of the CaF $(v, N, v', N') = (0, 0, 1, 0)$ transition to drive the clock transition.

Since the aim of the QSNET project is to search for possible temporal variations of fundamental constants (especially α and μ), clock comparison needs to be done between our CaF clock and atomic clocks at NPL. In the future, the clocks will be linked with optical fibres over distances of several hundred kilometers. The phase noise introduced in the optical fibre links will be canceled by setting up an interferometer with a fraction of light back-reflected from the far end of the fibre [65], and being compared against the incident light. Frequency combs at each end of the fibre will be used to measure the local clock frequency relative to the transfer laser. The exact frequency of the transfer laser cancels out in the ratio of the clock frequencies, which is proportional to the variations of the fundamental constants [62]. In the future, this clock aims at reaching the frequency fractional uncertainty at the 10^{-17} level according to our estimation of those uncertainties, then the clock will be one of the best molecular clock in the world, it will also contribute significantly towards establishing the frequency standard in the 17 μm frequency region.

Appendix A

Shape of wavelength modulated spectral lines

This appendix presents the mathematical model which is used to fit the wavelength modulated N₂O lines, details of the experiment are presented in Chapter 3. We derive an expression for the lineshape of an absorption feature obtained from wavelength modulation spectroscopy. Our analysis extends that found in Refs. [44, 45]. It captures the effects of Doppler broadening and pressure broadening, lineshape changes due to the modulation of the frequency, the effect of large optical depth, and the effect of simultaneous intensity and frequency modulation.

Let ω be the angular frequency of the laser, ω_c the centre frequency of the absorption feature, and γ a quantity representing the linewidth of the absorption feature. The laser current is modulated at frequency Ω and this modulates both the laser intensity and the laser frequency. We introduce a normalized detuning

$$\Delta = (\omega - \omega_c)/\gamma = \delta - \delta_m \cos(\Omega t + \Phi). \quad (\text{A.1})$$

Here, δ is the detuning of the laser averaged over a modulation cycle and δ_m is the modulation amplitude, both normalized to γ . The intensity of the light transmitted through the absorbing sample is $I_{\text{out}} = I_{\text{in}} \exp(-\alpha(\Delta))$ where I_{in} is the input intensity and α is the frequency-

dependent optical depth of the sample. We assume that the input intensity varies linearly with the frequency, $I_{\text{in}} = I_0(1 + p\delta - q\delta_m \cos(\Omega t))$, where I_0 is the intensity on resonance, p characterizes the intensity change due to a dc (or slowly-varying) offset, and q characterizes the intensity change due to the modulation. Φ is a phase shift between the modulation of the frequency and the intensity. With these definitions, the transmitted intensity is

$$I_{\text{out}}(\Delta, t) = I_0 (1 + p\delta - q\delta_m \cos(\Omega t)) \exp(-\alpha(\Delta)). \quad (\text{A.2})$$

We choose to re-write this in the form

$$I_{\text{out}}(\Delta, t) = g_1(\Delta, t) + g_2(\Delta, t), \quad (\text{A.3})$$

where

$$g_1(\Delta, t) = I_0 c_1 \exp(-\alpha(\Delta)) \quad (\text{A.4})$$

$$g_2(\Delta, t) = I_0 c_2 \exp(-\alpha(\Delta)) \quad (\text{A.5})$$

and

$$c_1 = p\Delta \quad (\text{A.6})$$

$$c_2 = 1 - 2p\delta_m \sin(\Phi/2) \sin(\Omega t + \Phi/2) + (p - q)\delta_m \cos(\Omega t). \quad (\text{A.7})$$

Our aim is to find the component of I_{out} oscillating at frequency $n\Omega$, where n is an integer, since this is the output of the lock-in amplifier. To do this, we first take the Fourier transform of $I_{\text{out}}(\Delta)$, which we denote $S(\tau)$:

$$S(\tau, t) = [G_1(\tau) + G_2(\tau)] \exp(-i\delta_m \tau \cos(\Omega t + \Phi)). \quad (\text{A.8})$$

Here, $G_1(\tau)$ and $G_2(\tau)$ are the Fourier transforms of $g_1(\delta)$ and $g_2(\delta)$ and we have used the shift theorem of Fourier transforms. Next, we use the Jacobi-Anger expansion which has the general

form $e^{iz \cos \theta} = J_0(z) + 2 \sum_{n=1}^{\infty} i^n J_n(z) \cos(n\theta)$, where J_n is the Bessel function of the first kind. Applying this to Eq.(A.8) and using $J_n(-z) = (-1)^n J_n(z)$ we get

$$S(\tau, t) = [G_1(\tau) + G_2(\tau)] \sum_{n=0}^{\infty} \epsilon_n (-i)^n J_n(\delta_m \tau) \cos[n(\Omega t + \Phi)], \quad (\text{A.9})$$

where $\epsilon_0 = 1$ and $\epsilon_n = 2$ for all $n > 0$. We now take the inverse Fourier transform, noting that the cosine factor does not depend on τ , to obtain

$$I_{\text{out}}(\delta, t) = s_1(\delta, t) + s_2(\delta, t) \quad (\text{A.10})$$

where

$$s_k(\delta, t) = \sum_{n=0}^{\infty} s_{k,n}(\delta) \cos[n(\Omega t + \Phi)], \quad (\text{A.11})$$

and

$$s_{k,n}(\delta) = \epsilon_n (-i)^n \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\delta\tau} J_n(\delta_m \tau) G_k(\tau) d\tau. \quad (\text{A.12})$$

The integral in Eq. (A.12) is the inverse Fourier transform of the product of J_n and G_k . Applying the convolution theorem, this can be written as

$$s_{k,n}(\delta) = \epsilon_n (-i)^n \frac{1}{\delta_m} \int_{-\infty}^{\infty} j_n \left(\frac{\delta'}{\delta_m} \right) g_k(\delta - \delta') d\delta', \quad (\text{A.13})$$

where j_n is the Fourier transform of the Bessel function, $j_n(x) = 2(-i)^n \cos(n \cos^{-1}(x)) / \sqrt{1-x^2}$ for $|x| < 1$ and zero otherwise. So we have

$$s_{k,n} = 2\epsilon_n (-1)^n \int_{-\delta_m}^{\delta_m} \frac{\cos(n \cos^{-1}(\delta'/\delta_m))}{\sqrt{\delta_m^2 - \delta'^2}} g_k(\delta - \delta') d\delta'. \quad (\text{A.14})$$

The decomposition into a sum of harmonics of Ω is complicated by the presence of trigonometric

functions of Ωt in the expression for c_2 , Eq. (A.7). This can be rewritten using

$$\begin{aligned}
c_2 \cos[n(\Omega T + \Phi)] &= \cos[n(\Omega T + \Phi)] \\
&+ \frac{1}{2} \delta_m p (\cos[(n-1)(\Omega T + \Phi)] + \cos[(n+1)(\Omega T + \Phi)]) \\
&- \frac{1}{2} \delta_m q (\cos[(n-1)\Omega T + n\Phi] + \cos[(n+1)\Omega T + n\Phi]) .
\end{aligned} \tag{A.15}$$

This shows that the term oscillating at $n\Omega$ will have contributions from $s_{2,n\pm 1}$ as well as from $s_{2,n}$.

These equations can be used to determine the lineshape in the most general cases. In the case where the intensity and frequency oscillate in phase ($\Phi = 0$) and the intensity changes in the same way for slow and fast changes ($p = q$), the result simplifies because $c_2 = 1$. In this case, the component of the output signal oscillating at frequency $n\Omega$ is

$$\frac{I_{\text{out},n}}{I_0} = 2\epsilon_n (-1)^n \int_{-\delta_m}^{\delta_m} \frac{\cos\left(n \cos^{-1}\left(\frac{\delta'}{\delta_m}\right)\right)}{\sqrt{\delta_m^2 - \delta'^2}} (1 + p\delta - p\delta') e^{-\alpha(\delta - \delta')} d\delta'. \tag{A.16}$$

The function $\alpha(\delta)$ should be chosen according to the dominant broadening mechanisms. In this work, we have used the Voigt function for fitting the 2f demodulated N₂O spectra.

A.1 Table of measured N₂O lines

iso	wn (observed)	wn (ht)	wn (nist)	o-ht	o-nist	f(observed)	v1'	v2'	l'	v3'	v1	v2	l	v3	PQR	J'	J	p	ov	amp
	cm ⁻¹	cm ⁻¹	cm ⁻¹	cm ⁻¹	cm ⁻¹	MHz														Arbitrary units
44	580.272780(098)	580.27260	580.403216 580.409125	0.000180	0.000000 -0.000106	17.3961403	0	1	1	0	0	0	0	0	P	4	5	e	s	0.0039
41	580.294380(101)	580.29432		0.000060		17.3967879	0	4	0	0	0	3	1	0	R	8	7	e	s	0.0004
41	580.403216(098)	580.40323		-0.000015		17.4000507	0	1	1	0	0	0	0	0	P	9	10	e	s	1.6335
41	580.409019(099)	580.40913		-0.000111		17.4002246	1	1	1	0	1	0	0	0	P	17	18	e	s	0.0051
43	580.459383(102)	580.45934		0.000043		17.4017345	0	1	1	0	0	0	0	0	P	5	6	e	s	0.0019
42	580.466629(102)	580.46661		0.000019		17.4019518	0	1	1	0	0	0	0	0	R	6	5	e	s	0.0024
41	580.489628(116)	580.48964		-0.000012		17.4026412	0	3	1	0	0	2	2	0	R	11	10	e	s	0.0012
41	580.591669(134)	580.59218		-0.000511		17.4057004	0	2	2	0	0	1	1	0	P	9	10	f	s	0.0824
42	580.640513(130)	580.64099		-0.000477		17.4071647	0	2	2	0	0	1	1	0	R	6	5	f	s	0.0003
42	580.665053(129)	580.66533		-0.000277		17.4079003	0	2	2	0	0	1	1	0	R	6	5	e	s	0.0001
45	580.676511(137)	580.67613		0.000381		17.4082439	0	1	1	0	0	0	0	0	P	6	7	e	s	0.0006
41	580.679905(120)	580.67969		0.000215		17.4083456	0	2	2	0	0	1	1	0	P	9	10	e	s	0.0820
41	580.687841(120)	580.68743		0.000411		17.4085835	0	3	1	0	0	2	2	0	R	11	10	f	s	0.0015
42	580.798609(122)	580.79890		-0.000291		17.4119043	0	2	0	0	0	1	1	0	R	14	13	e	s	0.0001
41	580.814320(111)	580.81411		0.000210		17.4123753	0	3	3	0	0	2	2	0	P	9	10	e	o	0.0045
41	580.814320(111)	580.81494		-0.000620		17.4123753	0	3	3	0	0	2	2	0	P	9	10	f	o	0.0045
41	580.935105(106)	580.93517		-0.000065		17.4159963	0	3	1	0	0	2	0	0	Q	1	1	e	s	0.0018
41	580.939720(105)	580.93980		-0.000080		17.4161347	0	3	1	0	0	2	0	0	Q	2	2	e	s	0.0046
41	580.946644(105)	580.94675		-0.000106		17.4163422	0	3	1	0	0	2	0	0	Q	3	3	e	s	0.0103
41	580.955991(105)	580.95602		-0.000029		17.4166225	0	3	1	0	0	2	0	0	Q	4	4	e	s	0.0103
41	580.967635(103)	580.96762		0.000015		17.4169715	0	3	1	0	0	2	0	0	Q	5	5	e	s	0.0119
41	580.975060(110)	580.97595		-0.000890		17.4171941	0	4	4	0	0	3	3	0	P	9	10	f	s	0.0030
41	580.977014(119)	580.97621		0.000804		17.4172527	0	4	4	0	0	3	3	0	P	9	10	e	s	0.0019
41	580.981594(102)	580.98155		0.000044		17.4173900	0	3	1	0	0	2	0	0	Q	6	6	e	s	0.0170
41	580.997890(103)	580.99780		0.000090		17.4178786	0	3	1	0	0	2	0	0	Q	7	7	e	s	0.0180
41	581.016500(102)	581.01640		0.000100		17.4184365	0	3	1	0	0	2	0	0	Q	8	8	e	s	0.0187
41	581.037390(101)	581.03733		0.000060		17.4190627	0	3	1	0	0	2	0	0	Q	9	9	e	s	0.0202
41	581.045788(101)	581.04559	581.045815	0.000198	-0.000027	17.4193145	0	2	0	0	0	1	1	0	R	2	1	e	s	0.0103

41	581.060616(115)	581.06062		-0.000004		17.4197590	0	3	1	0	0	2	0	0	Q	10	10	e	s	0.0240
44	581.062542(117)	581.06226		0.000282		17.4198168	0	1	1	0	0	0	0	0	P	3	4	e	s	0.0006
41	581.065240(131)	581.06450		0.000740		17.4198977	0	4	2	0	0	3	3	0	R	20	19	f	s	0.0016
41	581.086009(105)	581.08626		-0.000251		17.4205203	0	3	1	0	0	2	0	0	Q	11	11	e	s	0.0276
41	581.094567(114)	581.09753		-0.002963		17.4207769	0	4	2	0	0	3	3	0	R	20	19	e	s	0.0005
41	581.114122(102)	581.11427		-0.000148		17.4213631	0	3	1	0	0	2	0	0	Q	12	12	e	s	0.0257
41	581.144577(101)	581.14465		-0.000073		17.4222761	0	3	1	0	0	2	0	0	Q	13	13	e	s	0.0254
41	581.151653(105)	581.15140		0.000253		17.4224883	0	4	0	0	0	3	1	0	R	9	8	e	s	0.0011
41	581.177273(103)	581.17741		-0.000137		17.4232563	0	3	1	0	0	2	0	0	Q	14	14	e	s	0.0270
41	581.185699(117)	581.18565		0.000049		17.4235089	1	2	2	0	1	1	1	0	P	15	16	f	s	0.0007
43	581.187960(119)	581.18819		-0.000230		17.4235767	0	2	0	0	0	1	1	0	R	8	7	e	s	0.0020
41	581.212526(099)	581.21257		-0.000044		17.4243132	0	3	1	0	0	2	0	0	Q	15	15	e	s	0.0278
41	581.236040(128)	581.23593	581.235921	0.000110	0.000119	17.4250183	1	1	1	0	1	0	0	0	P	16	17	e	s	0.0094
41	581.238050(109)	581.23806	581.238050	-0.000014	0.000000	17.4250784	0	1	1	0	0	0	0	0	P	8	9	e	s	1.4866
41	581.250108(110)	581.25012		-0.000012		17.4254399	0	3	1	0	0	2	0	0	Q	16	16	e	s	0.0274
43	581.267218(096)	581.26721		0.000008		17.4259528	0	1	1	0	0	0	0	0	P	4	5	e	s	0.0031
41	581.290115(096)	581.29009		0.000025		17.4266392	0	3	1	0	0	2	0	0	Q	17	17	e	s	0.0300
42	581.306275(097)	581.30626		0.000015		17.4271237	0	1	1	0	0	0	0	0	R	7	6	e	s	0.0071
41	581.316089(097)	581.31608		0.000009		17.4274179	0	3	1	0	0	2	2	0	R	12	11	e	s	0.0030
41	581.332543(097)	581.33247		0.000073		17.4279112	0	3	1	0	0	2	0	0	Q	18	18	e	s	0.0282
41	581.377275(099)	581.37730		-0.000025		17.4292522	0	3	1	0	0	2	0	0	Q	19	19	e	s	0.0311
41	581.424507(100)	581.42457		-0.000063		17.4306682	0	3	1	0	0	2	0	0	Q	20	20	e	s	0.0360
41	581.428922(100)	581.42911		-0.000188		17.4308006	0	2	2	0	0	1	1	0	P	8	9	f	s	0.0855
41	581.461740(107)	581.46176		-0.000020		17.4317844	1	2	0	0	1	1	1	0	Q	30	30	f	s	0.0026
41	581.474371(103)	581.47429		0.000081		17.4321631	0	3	1	0	0	2	0	0	Q	21	21	e	s	0.0285
42	581.482067(110)	581.48236		-0.000293		17.4323938	0	2	2	0	0	1	1	0	R	7	6	f	s	0.0006
45	581.487453(118)	581.48729		0.000163		17.4325553	0	1	1	0	0	0	0	0	P	5	6	e	s	0.0001
41	581.500515(106)	581.50063		-0.000115		17.4329469	0	2	2	0	0	1	1	0	P	8	9	e	s	0.0895
42	581.515805(120)	581.51650	581.515805	-0.000695		17.4334053	0	2	2	0	0	1	1	0	R	7	6	e	s	0.0001
41	581.520688(122)	581.52091		-0.000222		17.4335516	1	2	0	0	1	1	1	0	Q	27	27	f	s	0.0001
41	581.526320(106)	581.52649		-0.000170		17.4337205	0	3	1	0	0	2	0	0	Q	22	22	e	s	0.0248
41	581.538106(126)	581.53846		-0.000354		17.4340738	1	2	0	0	1	1	1	0	Q	26	26	f	s	0.0002

41	581.549688(103)	581.55002		-0.000332		17.4344210	0	3	1	0	0	2	2	0	R	12	11	f	s	0.0030
41	581.554614(104)	581.55499		-0.000376		17.4345687	1	2	0	0	1	1	1	0	Q	25	25	f	s	0.0003
41	581.570054(104)	581.57055		-0.000496		17.4350316	1	2	0	0	1	1	1	0	Q	24	24	f	s	0.0001
41	581.580833(102)	581.58116		-0.000327		17.4353547	0	3	1	0	0	2	0	0	Q	23	23	e	s	0.0173
41	581.584758(104)	581.58517		-0.000412		17.4354724	1	2	0	0	1	1	1	0	Q	23	23	f	s	0.0005
41	581.598454(104)	581.59890		-0.000446		17.4358830	1	2	0	0	1	1	1	0	Q	22	22	f	s	0.0001
41	581.611277(105)	581.61176		-0.000483		17.4362674	1	2	0	0	1	1	1	0	Q	21	21	f	s	0.0002
41	581.623229(114)	581.62379		-0.000561		17.4366258	1	2	0	0	1	1	1	0	Q	20	20	f	s	0.0001
41	581.634609(101)	581.63502		-0.000411		17.4369669	1	2	0	0	1	1	1	0	Q	19	19	f	s	0.0004
41	581.638073(101)	581.63833		-0.000257		17.4370707	0	3	1	0	0	2	0	0	Q	24	24	e	s	0.0187
41	581.644333(101)	581.64460		-0.000267		17.4372584	0	3	3	0	0	2	2	0	P	8	9	e	o	0.0071
41	581.644333(101)	581.64520		-0.000867		17.4372584	0	3	3	0	0	2	2	0	P	8	9	f	o	0.0071
41	581.654709(104)	581.65522		-0.000511		17.4375695	1	2	0	0	1	1	1	0	Q	17	17	f	s	0.0001
42	581.659056(103)	581.65965		-0.000594		17.4376998	0	2	0	0	0	1	1	0	R	15	14	e	s	0.0001
41	581.663774(102)	581.66426		-0.000486		17.4378413	1	2	0	0	1	1	1	0	Q	16	16	f	s	0.0010
41	581.672070(104)	581.67261		-0.000540		17.4380899	1	2	0	0	1	1	1	0	Q	15	15	f	s	0.0001
41	581.679809(115)	581.68031		-0.000501		17.4383220	1	2	0	0	1	1	1	0	Q	14	14	f	s	0.0002
41	581.686818(115)	581.68739		-0.000572		17.4385321	1	2	0	0	1	1	1	0	Q	13	13	f	s	0.0002
41	581.693398(115)	581.69386		-0.000462		17.4387294	1	2	0	0	1	1	1	0	Q	12	12	f	s	0.0005
41	581.697576(115)	581.69801		-0.000434		17.4388546	0	3	1	0	0	2	0	0	Q	25	25	e	s	0.0158
41	581.704514(107)	581.70508		-0.000566		17.4390626	1	2	0	0	1	1	1	0	Q	10	10	f	s	0.0015
41	581.709271(108)	581.70986		-0.000589		17.4392052	1	2	0	0	1	1	1	0	Q	9	9	f	s	0.0002
41	581.713778(111)	581.71412		-0.000342		17.4393403	1	2	0	0	1	1	1	0	Q	8	8	f	s	0.0001
41	581.717580(110)	581.71787		-0.000290		17.4394543	1	2	0	0	1	1	1	0	Q	7	7	f	s	0.0001
41	581.720964(113)	581.72112		-0.000156		17.4395558	1	2	0	0	1	1	1	0	Q	6	6	f	s	0.0001
41	581.759976(097)	581.76021		-0.000234		17.4407253	0	3	1	0	0	2	0	0	Q	26	26	e	s	0.0157
41	581.771556(097)	581.77210		-0.000544		17.4410725	0	3	1	0	0	2	0	0	R	1	0	e	s	0.0021
41	581.806173(105)	581.80751		-0.001337		17.4421103	0	4	4	0	0	3	3	0	P	8	9	f	o	0.0002
41	581.806173(105)	581.80771		-0.001537		17.4421103	0	4	4	0	0	3	3	0	P	8	9	e	o	0.0002
41	581.824473(096)	581.82494		-0.000467		17.4426589	0	3	1	0	0	2	0	0	Q	27	27	e	s	0.0149
44	581.852146(098)	581.85230		-0.000154		17.4434885	0	1	1	0	0	0	0	0	P	2	3	e	s	0.0003
41	581.888125(099)	581.88838	581.888602	-0.000255	-0.000477	17.4445671	0	2	0	0	0	1	1	0	R	3	2	e	s	0.0256

41	581.891909(099)	581.89222	-0.000311	17.4446806	0	3	1	0	0	2	0	0	Q	28	28	e	s	0.0146
41	581.927927(106)	581.92818	-0.000253	17.4457604	0	4	2	0	0	3	1	0	Q	29	29	f	o	0.0007
41	581.927927(106)	581.92841	-0.000483	17.4457604	0	4	2	0	0	3	1	0	Q	28	28	f	o	0.0007
41	581.929121(111)	581.92910	0.000021	17.4457962	0	4	2	0	0	3	1	0	Q	30	30	f	o	0.0010
41	581.929121(111)	581.92969	-0.000569	17.4457962	0	4	2	0	0	3	1	0	Q	27	27	f	o	0.0010
41	581.931220(107)	581.93126	-0.000040	17.4458591	0	4	2	0	0	3	1	0	Q	31	31	f	o	0.0027
41	581.931220(107)	581.93192	-0.000700	17.4458591	0	4	2	0	0	3	1	0	Q	26	26	f	o	0.0027
41	581.934474(106)	581.93477	-0.000296	17.4459566	0	4	2	0	0	3	1	0	Q	32	32	f	o	0.0031
41	581.934474(106)	581.93501	-0.000536	17.4459566	0	4	2	0	0	3	1	0	Q	25	25	f	o	0.0031
41	581.938744(109)	581.93886	-0.000116	17.4460847	0	4	2	0	0	3	1	0	Q	24	24	f	o	0.0013
41	581.938744(109)	581.93972	-0.000976	17.4460847	0	4	2	0	0	3	1	0	Q	33	33	f	o	0.0013
41	581.943147(109)	581.94338	-0.000233	17.4462167	0	4	2	0	0	3	1	0	Q	23	23	f	s	0.0015
41	581.945491(109)	581.94620	-0.000709	17.4462869	0	4	2	0	0	3	1	0	Q	34	34	f	o	0.0009
41	581.945491(109)	581.94731	-0.001819	17.4462869	0	4	2	0	0	3	3	0	R	21	20	e	o	0.0009
41	581.948281(109)	581.94848	-0.000199	17.4463705	0	4	2	0	0	3	1	0	Q	22	22	f	s	0.0005
41	581.953805(138)	581.95406	-0.000255	17.4465362	0	4	2	0	0	3	1	0	Q	21	21	f	o	0.0007
41	581.953805(138)	581.95432	-0.000515	17.4465362	0	4	2	0	0	3	1	0	Q	35	35	f	o	0.0007
41	581.959731(139)	581.96005	-0.000319	17.4467138	0	4	2	0	0	3	1	0	Q	20	20	f	s	0.0002
41	581.961634(139)	581.96205	-0.000416	17.4467709	0	3	1	0	0	2	0	0	Q	29	29	e	s	0.0117
41	581.966237(140)	581.96634	-0.000103	17.4469089	0	4	2	0	0	3	1	0	Q	19	19	f	s	0.0023
41	581.972770(130)	581.97287	-0.000100	17.4471047	0	4	2	0	0	3	1	0	Q	18	18	f	s	0.0004
41	581.975167(131)	581.97582	-0.000653	17.4471766	0	4	2	0	0	3	1	0	Q	37	37	f	s	0.0005
41	581.979488(131)	581.97955	-0.000062	17.4473061	0	4	2	0	0	3	1	0	Q	17	17	f	s	0.0005
41	581.986243(144)	581.98631	-0.000067	17.4475086	0	4	2	0	0	3	1	0	Q	16	16	f	s	0.0005
41	581.988735(144)	581.98938	-0.000645	17.4475833	0	4	2	0	0	3	1	0	Q	38	38	f	s	0.0005
41	581.993025(144)	581.99307	-0.000045	17.4477120	0	4	2	0	0	3	1	0	Q	15	15	f	s	0.0005
41	581.999609(123)	581.99976	-0.000151	17.4479093	0	4	2	0	0	3	1	0	Q	14	14	f	s	0.0006
41	582.004116(128)	582.00494	-0.000824	17.4480444	0	4	2	0	0	3	1	0	Q	39	39	f	s	0.0002
41	582.006152(124)	582.00631	-0.000158	17.4481055	0	4	2	0	0	3	1	0	Q	13	13	f	s	0.0006
43	582.009828(114)	582.01011	-0.000282	17.4482157	0	2	0	0	0	1	1	0	R	9	8	e	o	0.0012
41	582.009828(114)	582.01031	-0.000482	17.4482157	0	4	0	0	0	3	1	0	R	10	9	e	o	0.0012
41	582.012527(114)	582.01267	-0.000143	17.4482966	0	4	2	0	0	3	1	0	Q	12	12	f	s	0.0011

41	582.017092(115)	582.01719		-0.000098		17.4484335	1	2	2	0	1	1	1	0	P	14	15	f	s	0.0015
41	582.018532(114)	582.01877		-0.000238		17.4484766	0	4	2	0	0	3	1	0	Q	11	11	f	s	0.0008
41	582.022284(123)	582.02257		-0.000286		17.4485891	0	4	2	0	0	3	1	0	Q	40	40	f	s	0.0017
41	582.024284(118)	582.02456		-0.000276		17.4486491	0	4	2	0	0	3	1	0	Q	10	10	f	s	0.0008
41	582.029921(118)	582.02998		-0.000059		17.4488181	0	4	2	0	0	3	1	0	Q	9	9	f	s	0.0005
41	582.034291(117)	582.03446		-0.000169		17.4489491	0	3	1	0	0	2	0	0	Q	30	30	e	s	0.0122
41	582.039516(105)	582.03957		-0.000054		17.4491057	0	4	2	0	0	3	1	0	Q	7	7	f	s	0.0004
41	582.042234(107)	582.04236		-0.000126		17.4491872	0	4	2	0	0	3	1	0	Q	41	41	f	s	0.0008
41	582.043426(107)	582.04365		-0.000224		17.4492229	0	4	2	0	0	3	1	0	Q	6	6	f	s	0.0014
41	582.046956(107)	582.04721		-0.000254		17.4493287	0	4	2	0	0	3	1	0	Q	5	5	f	s	0.0018
41	582.050008(111)	582.05022		-0.000212		17.4494203	0	4	2	0	0	3	1	0	Q	4	4	f	s	0.0022
41	582.052152(113)	582.05266		-0.000508		17.4494845	0	4	2	0	0	3	1	0	Q	3	3	f	s	0.0014
41	582.054220(113)	582.05450		-0.000280		17.4495465	0	4	2	0	0	3	1	0	Q	2	2	f	s	0.0002
41	582.063118(105)	582.06321	582.063199	-0.000092	-0.000081	17.4498133	1	1	1	0	1	0	0	0	P	15	16	e	s	0.0025
41	582.073253(104)	582.07327	582.073253	-0.000014	0.000000	17.4501171	0	1	1	0	0	0	0	0	P	7	8	e	s	1.3931
41	582.079876(155)	582.07998		-0.000104		17.4503157	0	4	2	0	0	3	1	0	Q	4	4	e	s	0.0011
41	582.091695(137)	582.09186		-0.000165		17.4506700	0	4	2	0	0	3	1	0	Q	5	5	e	s	0.0006
41	582.105832(102)	582.10612		-0.000288		17.4510938	0	4	2	0	0	3	1	0	Q	6	6	e	s	0.0014
41	582.109215(101)	582.10945		-0.000235		17.4511952	0	3	1	0	0	2	0	0	Q	31	31	e	s	0.0128
41	582.122526(103)	582.12275		-0.000224		17.4515943	0	4	2	0	0	3	1	0	Q	7	7	e	s	0.0003
41	582.141047(105)	582.14124		-0.000193		17.4521495	0	3	1	0	0	2	2	0	R	13	12	e	s	0.0016
42	582.145835(105)	582.14614		-0.000305		17.4522931	0	1	1	0	0	0	0	0	R	8	7	e	s	0.0052
41	582.162889(108)	582.16313		-0.000241		17.4528043	0	4	2	0	0	3	1	0	Q	9	9	e	s	0.0004
41	582.186785(112)	582.18703		-0.000245		17.4535207	0	3	1	0	0	2	0	0	Q	32	32	e	s	0.0123
41	582.212747(114)	582.21299		-0.000243		17.4542990	0	4	2	0	0	3	1	0	Q	11	11	e	s	0.0007
41	582.241277(116)	582.24147		-0.000193		17.4551544	0	4	2	0	0	3	1	0	Q	12	12	e	s	0.0011
41	582.265908(108)	582.26640		-0.000492		17.4558928	0	2	2	0	0	1	1	0	P	7	8	f	s	0.0603
41	582.266871(109)	582.26721		-0.000339		17.4559216	0	3	1	0	0	2	0	0	Q	33	33	e	s	0.0066
41	582.271872(110)	582.27232		-0.000448		17.4560716	0	4	2	0	0	3	1	0	Q	13	13	e	s	0.0040
41	582.305078(114)	582.30553		-0.000452		17.4570671	0	4	2	0	0	3	1	0	Q	14	14	e	s	0.0015
41	582.323201(132)	582.32355		-0.000349		17.4576104	0	2	2	0	0	1	1	0	P	7	8	e	s	0.0553
41	582.340790(138)	582.34111		-0.000320		17.4581377	0	4	2	0	0	3	1	0	Q	15	15	e	s	0.0004

41	582.349705(134)	582.35002	-0.000315	17.4584049	0	3	1	0	0	2	0	0	Q	34	34	e	s	0.0037
42	582.369249(180)	582.36954	-0.000291	17.4589909	0	2	2	0	0	1	1	0	R	8	7	e	s	0.0002
41	582.378885(177)	582.37905	-0.000165	17.4592797	0	4	2	0	0	3	1	0	Q	16	16	e	s	0.0004
41	582.414368(150)	582.41438	-0.000012	17.4603435	0	3	1	0	0	2	2	0	R	13	12	f	s	0.0011
41	582.419100(152)	582.41935	-0.000250	17.4604854	0	4	2	0	0	3	1	0	Q	17	17	e	s	0.0011
41	582.435321(153)	582.43544	-0.000119	17.4609716	0	3	1	0	0	2	0	0	Q	35	35	e	s	0.0025
41	582.461529(138)	582.46200	-0.000471	17.4617573	0	4	2	0	0	3	1	0	Q	18	18	e	s	0.0002
41	582.475740(134)	582.47616	-0.000420	17.4621834	0	3	3	0	0	2	2	0	P	7	8	e	o	0.0027
41	582.475740(134)	582.47649	-0.000750	17.4621834	0	3	3	0	0	2	2	0	P	7	8	f	o	0.0027

Table A.1: A complete table of measured N₂O transitions.

Tab. A.1 presents all the N_2O transitions measured in our experiment. iso is the code used in HITRAN [3] to identify isotopes; for N_2O , 41 means $^{14}\text{N}_2^{16}\text{O}$, 42 means $^{14}\text{N}^{15}\text{N}^{16}\text{O}$, 43 means $^{15}\text{N}^{14}\text{N}^{16}\text{O}$, 44 means $^{14}\text{N}_2^{18}\text{O}$ and 45 means $^{14}\text{N}_2^{17}\text{O}$. $\text{cm}^{-1}(\text{c})$ means HITRAN transition wavenumbers, wn (observed) means the measured transition wavenumbers. o-ht is the difference between our measured wavenumbers and those in HITRAN database, most lines have a frequency difference smaller than 15 MHz, and o-nist is the difference between our measured transitions and those in NIST database [36]. The quantum labels used from the 8th to 18th columns are the quantum numbers for describing N_2O . PQR is the branch of the transition: P means $J' < J$, Q means $J' = J$ and R means $R' < R$, and J' and J are the rotational angular momenta of the upper and lower vibrational states. ov means if the line is overlapped with other lines, s means no overlap and o means overlap: several lines share same fitting parameters. amp is the fitted amplitude value using Voigt line profile.

Appendix B

The Arduino script for the injection relocker

This appendix presents the Arduino control script for the v2 and v3 injection relockers, the details about the relockers are in Chapter 4. All the files below must be in a same folder, the folder name should be the same as the main control file.

main.ino

```
// constants
```

```
// pin setting
```

```
const int triggerPin = A0; // input, cavity ramp TTL
const int cavityPin = A1;  // input, photodiode signal
const int outPin = DAC1;   // output, signal for locking
const int messagePin = 45; // output, send message signal to experiment if unlock
const int redLED = 12;     // red LED, HIGH when scanning
const int greenLED = 11;   // green LED, HIGH when locked
const int switchPin = 10;  // a switch to control manual and automatic modes
```

```
// Serial setting
```

```
const int writeResolution = 12; // analog write resolution, 0-4095 for 12
```

```
const int readResolution = 12;    // analog read resolution, 0-4095 for 12
const int writeMax = 4096;
const int readMax = 4096;
const int serialSpeed = 115200;  // set data rate to xx bps

// manual and automatic modes switching
int switchState;                  // status of switch, 1 for HIGH (Automatic) and 0 for LOW (Man
int switchStateOld;              // another variable to record switch state

// analog out
int outValue = 0;
const int initOut = 1000;  // initial output

// peak detection
const int triggerThreshold = 600;  // the threshold used to find the rising slope of tr
const int peakNAvgScan = 1;  // how many points used in a scan to average for a cavity
const int peakNAvgCheck = 5;  // how many points used in monitoring the lock status to a
int peakValueTemp = 0;  // peak height, used in the main loop
int peakPosTemp = 0;  // peak position, used in the main loop
const int peakSide = 0;  // side points used near the peak value
int peakValue = 0;  // peak height, update in peakDetect
int peakPos = 0;  // peak position, update in peakDetect

long int rampWidth = 0;          // width of the positive ramp used to scan the cavity
const int peakPosUnc = 5;        // peak position uncertainty, percent

const int peakPercentScan = 60;  // peakPercent% of previous peak value is identified a
const int peakPercentCheck = 80; // peakPercent% of previous peak value is identified a

int peakMaxMin = 300;  // min value of a peak
```

```
// scan
int scanAdd = 100;          // scan region added before and after window region
int windowSize = 0; // length of the locked window, windowSize = windowEnd - windowStart
const int windowSizeMin = 30; // min size of the window
const int windowHeightThresh = 30; // min value of a window
int scanStart = 0;
int scanEnd = 4096;
const int autoScanAdd = 300; // points added before or after the lock window
int windowStart = 0;
int windowEnd = 0;
const int scanLeft = 50; // when the left threshold is found, how many points on the left
const int jumpDisAuto = 2; // jump distance in the first auto scan
const int jumpDisRelock = 3; // jump distance for relock

// for ramping voltage
const int rampNum = 100; // how many steps to ramp
const int rampDelay = 1; // in ms

// time
long int timeStart;
long int timeNow;
const int manualDelay = 1000; // delay used in manual mode in ms

//long int timeBetweenRelock = 10000; // if relocks happen multiple times in 10s, force scan
int relockNumMax = 10; // how many relock happen to force scan
int relockNum = 0;
//long int timeRelockStart = 0;

// lock status
bool ifLock = false;
```

```
void setup() {  
    // pinMode settings  
    pinMode(messagePin, OUTPUT);  
    pinMode(redLED, OUTPUT);  
    pinMode(greenLED, OUTPUT);  
    pinMode(switchPin, INPUT);  
  
    // analogRead and analogWrite settings  
    analogWriteResolution(writeResolution);  
    analogReadResolution(readResolution);  
  
    // Serial communication start  
    Serial.begin(serialSpeed);  
  
    switchState = digitalRead(switchPin);  
    if (switchState) {  
        scanStart = initOut - autoScanAdd;  
        scanEnd = initOut + autoScanAdd;  
        while (!ifLock) {  
            ifLock = scanAuto(jumpDisAuto);  
            scanStart = max(0, scanStart - autoScanAdd);  
            scanEnd = max(0, scanEnd + autoScanAdd);  
        }  
    } else {  
        outValue = initOut;  
        analogWrite(outPin, outValue);  
    }  
  
    // start count time  
    timeStart = millis();  
    Serial.println("start");  
}
```



```
}
```

```
void loop() {
```

```
    switchState = digitalRead(switchPin);
```

```
    // manual mode
```

```
    if (!switchState) {
```

```
        outValue = initOut;
```

```
        analogWrite(outPin, outValue);
```

```
        peakDetect(peakNAvgCheck);
```

```
        if ((checkLock(peakValueTemp, peakValue, peakPos, peakPosTemp, peakPercentCheck))) {
```

```
            ifLock = true;
```

```
        } else {
```

```
            ifLock = false;
```

```
        }
```

```
        peakValueTemp = peakValue;
```

```
        peakPosTemp = peakPos;
```

```
        switchStateOld = switchState;
```

```
        delay(manualDelay);
```

```
        return;
```

```
    }
```

```
    // from manual switch to automatic
```

```
    if ((switchState) && (!switchStateOld)) {
```

```
        // find the peak and put the output to the center of the locking window
```

```
        peakDetect(peakNAvgCheck);
```

```
        scanManual(peakValue, peakPos);
```

```
        switchStateOld = switchState;
```

```
    delay(manualDelay);
    return;
}

// automatic mode
if (ifLock) {
    peakDetect(peakNAvgCheck);
    // peakValue and peakPos update in peakDetect
    // peakValueTemp and peakPosTemp update in scan functions
    if ((checkLock(peakValueTemp, peakValue, peakPosTemp, peakPos, peakPercentCheck))) {
        return;
    } else {
        ifLock = false;
        if (jumpRelock()) {
            Serial.println("M: Relock by jumping successfully.");
            peakDetect(peakNAvgCheck);
            if (relockNum == 0) {
                //timeRelockStart = millis();
                relockNum += 1;
                ifLock = true;
            } else if (relockNum < relockNumMax) {
                relockNum += 1;
                ifLock = true;
            }
        } else {
            relockNum = 0; // reset relock number
            Serial.println("M: Scanning...");
            scanStart = max(windowStart - 2*scanAdd, 0);
            scanEnd = min(windowEnd + 2*scanAdd, writeMax);
            ifLock = scanAuto(jumpDisRelock);
        }
        //scanManual(peakValue, peakPos);
    }
}
```

```

        //ifLock = true;
        return;
    } else {
        relockNum = 0; // reset relock number
        ifLock = false;
        scanStart = max(windowStart - 2*scanAdd, 0);
        scanEnd = min(windowEnd + 2*scanAdd, writeMax);
        ifLock = scanAuto(jumpDisRelock);
        if (ifLock) {
            Serial.println("M: Relock by jumping failed, found the lock point by scan succ
        } else {
            Serial.println("M: Relock failed.");
        }
    }
}
} else {
    relockNum = 0; // reset relock number
    Serial.println("M: Scanning...");
    scanStart = initOut - 3*scanAdd;
    scanEnd = initOut + 3*scanAdd;
    ifLock = scanAuto(jumpDisAuto);
}
}

```

peakDetect.ino

```

// function for peak detection
// no return, update peak position and height inside
// peakNAvg: how many points to average for one output voltage

// constants only used here
// related constants defined outside
/*

```

```
long int timeNow;
bool ifLock = false;
const int peakSide = 0; // side points used near the peak value
int peakValue = 0; // peak height, update in peakDetect
int peakPos = 0; // peak position, update in peakDetect
*/

void peakDetect(int peakNAvg) {
    // using trigger value to find the positive ramp
    int triggerValue, triggerValueNew;

    int cavityMaxV = 0; // max cavity peak value during a ramp

    // time parameters
    long int tStart;
    long int tFromTrig;

    const int arraySize = 10000; // length of array used in this section

    // reset the position and height of the peak
    peakPos = 0;
    peakValue = 0;

    for (int i = 0; i < peakNAvg; i++) {
        int posIndex = 0; // index of the peak
        int cavityVs[arraySize];
        int count = 0;
        int peakPosi = 0; // temporary peak position, unit is time
        int cavityVsum = 0; // sum of cavity values
        int cavityMaxAvg = 0; // points around the max value
```

```

// read twice to capture the jumping point
triggerValue = analogRead(triggerPin)/triggerThreshold;
triggerValueNew = analogRead(triggerPin)/triggerThreshold;

// jump out when trigger value changes and it's on the positive side of the ramp
while ((triggerValue == triggerValueNew) || (triggerValueNew != 1)) {
    triggerValue = analogRead(triggerPin)/triggerThreshold;
    triggerValueNew = analogRead(triggerPin)/triggerThreshold;
}

tStart = micros();
while (analogRead(triggerPin)/triggerThreshold == 1) {
    cavityVs[count] = analogRead(cavityPin);
    cavityVsum += cavityVs[count];
    tFromTrig = micros() - tStart;

    if (cavityVs[count] > cavityMaxV) {
        cavityMaxV = cavityVs[count];
        peakPosi = tFromTrig;
        posIndex = count;
    }

    rampWidth = tFromTrig;
    triggerValue = analogRead(triggerPin)/triggerThreshold;
    count++;
}

for (int i = posIndex - peakSide; i < posIndex + peakSide + 1; i++) {
    cavityMaxAvg += cavityVs[i];
}

// remove background

```

```
cavityMaxAvg = cavityMaxAvg / (2*peakSide + 1) - cavityVsum / (count + 1);

if (cavityMaxAvg > peakValue) {
    peakValue = cavityMaxAvg;
    peakPos = peakPosi;
}
}

if (ifLock) {
    digitalWrite(greenLED, HIGH);
} else {
    digitalWrite(greenLED, LOW);
}

timeNow = millis() - timeStart;

Serial.print("ifLock:");
Serial.println(ifLock);

Serial.print("time:");
Serial.println(timeNow);

Serial.print("peak:");
Serial.println(peakValue);

Serial.print("peakPos:");
Serial.println(peakPos);

Serial.print("out:");
Serial.println(outValue);
}
```

scanManual.ino

```

// this function is only used when the system is locked manual

// constants defined in other files
/*
const int peakNAvgScan;
int windowStart = 0;
int windowEnd = 0;
const int scanLeft = 50; // when the left threshold is found, how many points on the le
*/

void scanManual(int peakValueIn, int peakPosIn) {
//void scanManual() {}
    // put red LED on when the scanning start

    digitalWrite(redLED, HIGH);

    // scan back to find the left limit

    while (ifLock) {
        // check switch state
        switchState = digitalRead(switchPin);
        if (!switchState) {
            digitalWrite(redLED, LOW);
            analogWrite(outPin, initOut);
            return;
        }

        analogWrite(outPin, outValue);
        peakDetect(peakNAvgScan);
        if ((checkLock(peakValueIn, peakValue, peakPosIn, peakPos, peakPercentCheck))) {
            outValue = outValue - 1;
        } else {

```

```
//windowStart = outValue;
ifLock = false;
}
}

// scan forward to find the right limit

bool windowOpen = true;
bool windowStartFlag = false;
outValue = max(outValue - scanLeft, 0); // to include the left edge
while (windowOpen) {
    // check switch state
    switchState = digitalRead(switchPin);
    if (!switchState) {
        digitalWrite(redLED, LOW);
        analogWrite(outPin, initOut);
        return;
    }

    analogWrite(outPin, outValue);
    peakDetect(peakNAvgScan);
    if ((checkLock(peakValueIn, peakValue, peakPosIn, peakPos, peakPercentScan))) {
        if (!windowStartFlag) {
            windowStartFlag = true;
            windowStart = outValue;
        }
    } else {
        if (windowStartFlag) {
            if (outValue - windowStart < windowSizeMin) {
                // to avoid drift around the edge
                windowStartFlag = false;
            }
        }
    }
}
```



```

        } else {
            windowOpen = false;
            windowEnd = outValue;
        }
    }
}

outValue = outValue + 1;
}

outValue = (windowStart + windowEnd) / 2;
windowSize = windowEnd - windowStart;
analogWrite(outPin, outValue);
ifLock = true;
delay(100);
peakDetect(peakNAvgCheck);

digitalWrite(redLED, LOW);
Serial.println("scanManual finish");
return;
}

```

checkLock.ino

```

// function for checking lock status, put peak position to highest priority, then peak v

bool checkLock(int oldPeakValue, int newPeakValue, long int oldPeakPos, long int newPeakPos) {

    int oldPeakThresh = map(peakPercent, 0, 100, 0, oldPeakValue);

    /*
    Serial.println("check lock:");
    Serial.print("oldPeakValue: ");
    Serial.println(oldPeakValue);
    */
}

```

```
Serial.print("newPeakValue: ");
Serial.println(newPeakValue);

Serial.print("oldPeakPos: ");
Serial.println(oldPeakPos);

Serial.print("newPeakPos: ");
Serial.println(newPeakPos);
*/

if (newPeakValue < peakMaxMin) {
    return false;
}

if ((newPeakValue >= oldPeakThresh)) {
    if ((abs(newPeakPos-oldPeakPos) < rampWidth * peakPosUnc / 100)) {
        if (newPeakValue - oldPeakValue > oldPeakValue/3) {
            // too high peak value, sometimes because of amplitude drift, update here
            peakValueTemp = newPeakValue*4/5;
            peakPosTemp = newPeakPos;
            return true;
        }

    } else {
        return false;
    }
    //return true;
} else {
    return false;
}
```

```
}
```

jumpRelock.ino

```
// paramters used here but defined outside
/*
int windowSize; // length of the locked window
int windowStart;
int windowEnd;
windowSize = windowEnd - windowStart; defined in scanManual

int peakValueTemp;
int peakPosTemp;
*/

bool jumpRelock() {
    // turn off green light when the laser gets unlocked
    digitalWrite(greenLED, LOW);

    // important: windowStart and windowEnd should be the actual start and end of the window
    // the slope on the righthand side should not be included!
    int jump = 1;
    int parity = 1;
    int windowCen = (windowEnd + windowStart)/2; // center of the window
    int moveStep = (windowEnd - windowStart)/2; // step of moving the output point
    int jumpThresh = 5; // threshold of the jumping distance (how many times)

    while (jump < jumpThresh){
        if (parity) {
            // move to right
            rampOut(min(windowCen + jump * moveStep, writeMax));
            delay(100);
            peakDetect(peakNAvgCheck);
        }
    }
}
```

```

    if (checkLock(peakValueTemp, peakValue, peakPosTemp, peakPos, peakPercentScan)) {
        // if relock success, update window position
        windowCen = windowCen + jump * moveStep;
        windowStart = max(windowCen - moveStep, scanAdd);
        windowEnd = min(windowCen + moveStep, writeMax - scanAdd);
        scanStart = windowStart - scanAdd;
        scanEnd = windowEnd + scanAdd;
        return true;
    }
    parity = parity - 1;
} else {
    // move to left
    rampOut(min(windowCen - jump * moveStep, writeMax));
    delay(100);
    peakDetect(peakNAvgCheck);
    if (checkLock(peakValueTemp, peakValue, peakPosTemp, peakPos, peakPercentScan)) {
        // if relock success, update window position
        windowCen = windowCen - jump * moveStep;
        windowStart = max(windowCen - moveStep, scanAdd);
        windowEnd = min(windowCen + moveStep, writeMax - scanAdd);
        scanStart = windowStart - scanAdd;
        scanEnd = windowEnd + scanAdd;
        return true;
    }
    parity = parity + 1;
    jump += 1; // update jump
}
}

return false; // try a scan if the lock region is not found by several jumps
}

```

scanAuto.ino

```
// only used when use auto scan

// const int jumpDis = 10; // related to scan speed, the distance between two points

//other constants
/*
const int initOut = 1000; // initial output
int peakMaxMin;
const int windowWidthThresh;
int scanStart = 0;
int scanEnd = 4096;
const int autoScanAdd = 150; // points added before or after the lock window
*/
bool scanAuto(int jumpDis) {
    // scanStart and scanEnd needs to be defined outside
    // update peakValueTemp and peakPosTemp here
    // put red LED on when the scanning start
    digitalWrite(redLED, HIGH);

    //scanStart = initOut - autoScanAdd;
    //scanEnd = initOut + autoScanAdd;

    // lists of peak height and peak positions
    int peakValueList[scanEnd - scanStart]; // list number incorrect but not important
    long int peakPosList[scanEnd - scanStart];
    int peakHeightFirst = 0; // peak height of the first point in the window (left)

    bool windowStartFlag = false;
    bool windowEndFlag = false;
    // reset
    windowStart = 0;
    windowEnd = 0;
```

```
int peakWindowPos = 0; // peak position in this window

// first jump some points to quickly find the lock window
int index = 0; // index used in the loop
int indexWindowStart = 0, indexWindowEnd = 0;
for (int i = scanStart; i < scanEnd; i = i+jumpDis) {
    // check switch state
    switchState = digitalRead(switchPin);
    if (!switchState) {
        digitalWrite(redLED, LOW);
        analogWrite(outPin, initOut);
        return true;
    }

    outValue = i;
    analogWrite(outPin, outValue);
    peakDetect(peakNAvgScan);
    peakValueList[index] = peakValue;
    peakPosList[index] = peakPos;

    if (windowStartFlag) {
        if ((abs(peakPosList[index]-peakWindowPos) < peakPosUnc*rampWidth/100) && (peakVal
    } else {
        if (i - windowStart > windowWidthThresh) {
            windowEnd = i;
            windowEndFlag = true;
            indexWindowEnd = index;
            i = scanEnd; // jump out
        } else {
            // if window is too narrow, reset
            windowStartFlag = false;
        }
    }
}
```

```

    }
} else {
    // start a new window
    // use peak position (main) and peakvalue to start a window
    if (peakValueList[index] < peakMaxMin) {
        continue;
    }

    if ((abs(peakPosList[index]-peakPosList[index-1]) < peakPosUnc*rampWidth/100) && (
        windowStart = i;
        peakWindowPos = peakPos;
        peakHeightFirst = peakValueList[index];
        windowStartFlag = true;
        indexWindowStart = index;
    }
}
index++;
}

// never start the window or never found the window with a good width
if (!windowStartFlag) {
    Serial.println("Locking window not found, try another scan.");
    scanStart = max(scanStart - 2*scanAdd, 0);
    scanEnd = min(scanEnd + 2*scanAdd, writeMax);
    return false;
}

// didn't reach the end of the window
if (windowStartFlag && !windowEndFlag) {
    Serial.println("Locking window not complete, try another scan.");
    return false;
}

```

```
// didnt' reach the start of the window
if (windowStart - scanStart < 5) {
    Serial.println("Locking window not complete, try another scan.");
    return false;
}

// found a full window
if (windowStartFlag && windowEndFlag) {
    // peak position, the complete window is included here
    int peakValueAvg = 0;
    int peakPosAvg = 0;
    // only take the height value in the flat area
    for (int i = indexWindowStart; i < (indexWindowStart + indexWindowEnd)/2; i++) {
        peakValueAvg += peakValueList[i];
        peakPosAvg += peakPosList[i];
    }
    peakValueAvg = peakValueAvg / (indexWindowEnd - indexWindowStart)/2;
    peakPosAvg = peakPosAvg / (indexWindowEnd - indexWindowStart)/2;

    peakValueTemp = peakValueAvg;
    peakPosTemp = peakPosAvg;

    // use scan manual to find the accurate range
    //scanManual(peakValueTemp, peakPosTemp);
    //outValue = (windowStart + windowEnd) / 2;
    //analogWrite(outPin, outValue);
    rampOut((windowStart + windowEnd)/2);
    delay(100);
    peakDetect(peakNAvgCheck);
    peakValueTemp = peakValue;
    peakPosTemp = peakPos;
```



```
    digitalWrite(redLED, LOW);

    return true;
}
}
```

rampOut.ino

```
// constants used here
/*
const int rampNum = 100;  // how many steps to ramp
const int rampDelay = 1;  // in ms
*/

void rampOut(int newOut) {
    int outTemp = 0;
    for (int i = 0; i < rampNum; i++) {
        outTemp = map(i, 0, rampNum, outValue, newOut);
        analogWrite(outPin, outTemp);
    }
    outValue = newOut;
    analogWrite(outPin, newOut);
}
```

Appendix C

Summary of Acronyms

Some frequently used acronyms used in this thesis are presented here.

- ACPF: ab initio calculation method: averaged coupled-pair function
- AMO: atomic, molecular and optical
- CCD: charged coupled device
- FSR: free spectral range
- FWHM: full width at half maximum
- HITRAN[7]: high-resolution transmission molecular absorption database
- MOT: magneto-optical trap
- NIST: National Institute of Standards and Technology (USA)
- NPL: National Physical Laboratory (UK)
- PDH lock: Pound-Drever-Hall lock
- PID: proportional-integral-derivative
- QCL: quantum cascade laser
- QSNET: a network of clocks for measuring the stability of fundamental constants

- RCCSC(T): ab initio calculation method: restricted coupled-cluster singles and doubles with perturbative triples
- WMS: wavelength modulation spectroscopy

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