An Introduction to Noise-Immune Cavity Enhanced Optical Heterodyne
Velocity Modulation Spectroscopy

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Introduction

The space between stars is far from empty; a myriad of chemical reactions take place every second. In cold and diffuse environments, these interstellar chemical reactions are dominated by the interactions between molecular ions and neutral molecules. Unlike neutral molecules, the majority of molecular ions are not naturally observed on Earth. This is due to the highly reactive nature of these molecular ions. Species such as CH_5^+, will immediately react with the nearest molecules, never being detected. The high reactivity of these molecular ions makes it necessary to develop techniques to produce and observe these molecules. Mid-infrared spectroscopy of positive column glow discharges is a common laboratory experiment used to measure the spectra of these ions of interest.

A positive column glow discharge is used to generate these highly reactive ions in a laboratory setting so that they can be studied on Earth. The basic concept of a positive column glow discharge is that a cell is filled with a gas mixture, and then the gas is ionized inside the cell to produce a plasma. This generates a sample that will contain the ions of interest. Unfortunately, a positive column is still unable to produce molecular ions in detectable quantities using conventional spectroscopic techniques. While a positive column is undoubtedly forming the ions of interest, the amount of neutral molecules also being produced in the discharge far outnumbers the ions. The goal of the McCall groups is to develop an instrumental technique that enhances these weak ionic signals and measure with the highest precision to date. The ultimate goal is for these measurements to be used by astronomers to aid them able to aid them in their search for these molecules in space.

Studying molecular ions is relevant to more than just astronomers. An ion such as H_3^+ is the simplest polyatomic molecule and is of great interest to theoretical and quantum chemists, who use it as a model system to test new theories and calculations. With the level of these theoretical calculations now reaching the level of experimental uncertainty, it is important to obtain highly precise spectroscopic measurements to push the limits of these calculations.

We have developed an instrumental technique to study molecular ions. This technique, known as Noise-Immune Cavity Enhanced Optical Heterodyne Velocity Modulation Spectroscopy (NICE-OHVMS), is a combination of three different types of spectroscopy that result in this "super" technique. Using NICE-OHVMS, we have measured the spectra of the several molecular ions to the highest precision ever recorded.

Part 1: Instrumentation

Experimental Instrumentation

All spectroscopy experiments require three things; a light source, a sample analyte, and a light detector. In a traditional UV-Vis spectroscopy experiment, as shown in Figure 1 the light source passes through the sample, which absorbs some of the light from the source. The light that is not absorbed by the sample passes through and is read by the detector. The amount of light that the sample absorbs is calculated by subtracting the intensity of the detected light (transmission) from the intensity of the light source before light reaches the sample. A typical absorption spectrum is shown in Figure 2. In UV-Vis spectroscopy, a molecular transition occurs after the molecule absorbs energy. This molecule becomes "excited" as the excess energy promotes an electron to move from a lower energy orbital to a higher energy orbital. The "transition" of the electron from the lower energy orbital to the higher energy orbital is what is

measured in the absorption spectrum. Electronic energy levels follow the equation E=hν, where E is the energy of the photon, h is Planck's constant, and ν is the frequency of the photon. The line shape of a traditional UV-Vis spectroscopy experiment looks Gaussian in nature due to inhomogeneous broadening effects. These broadening effects make it very difficult to determine a precise value for the line center using traditional approaches.
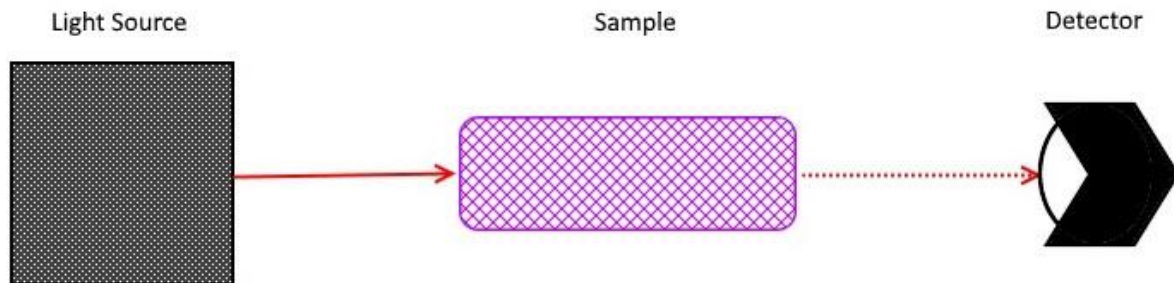
Figure 1: The main components of a traditional absorption spectroscopy experiment.

Traditional UV-Vis Absorption Spectrum

Intensity (a.u)

Wavelength (nm)
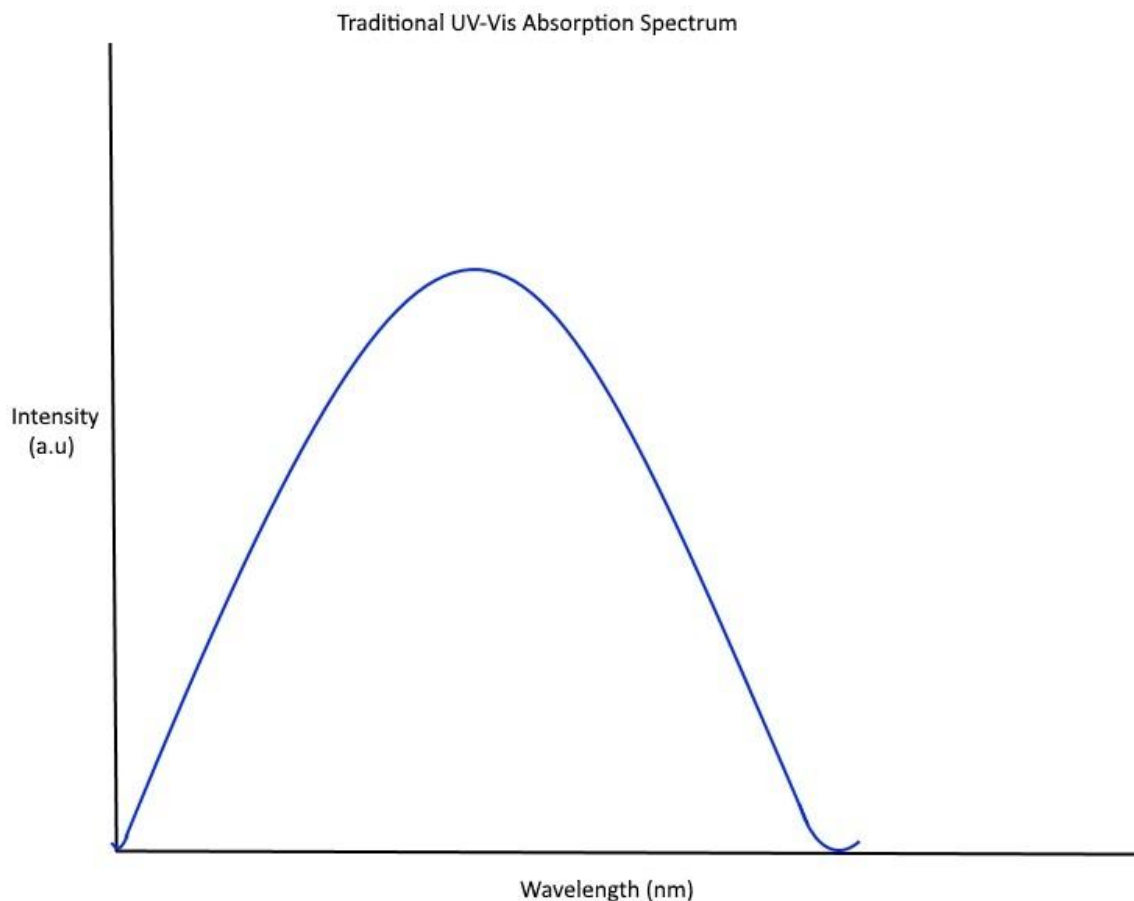
Figure 2: An example UV-Vis Spectrum.

The spectroscopy performed in the McCall group is focused in the mid-infrared region. This is different than UV-Vis spectroscopy because infrared light causes molecules to rotate and vibrate, resulting in ro-vibrational transitions. Ro-vibrational transitions are stimulated by photons or energy, in the same manner as UV-Vis spectroscopy. These ro-vibrational transitions occur when a photon moves from a lower or ground state to an upper or excited state. The difference in energy levels between electronic transitions and ro-vibrational transitions is shown in Figure 3. Ro-vibrational transitions are stimulated by photons that have less energy than those that stimulate electronic transitions. This makes light in the infrared region perfect for

stimulating these molecular vibrations. The ro-vibrational energy levels follow the form

E=BJ(J+1), where E is energy, B is the rotational constant of the molecule, and J is the total

rotational angular momentum quantum number. The line shape of vibrational transitions has the

same general characteristics as electronic transitions. The line shapes of transitions that are

produced in infrared spectroscopy experiments will be discussed in more detail in later sections.
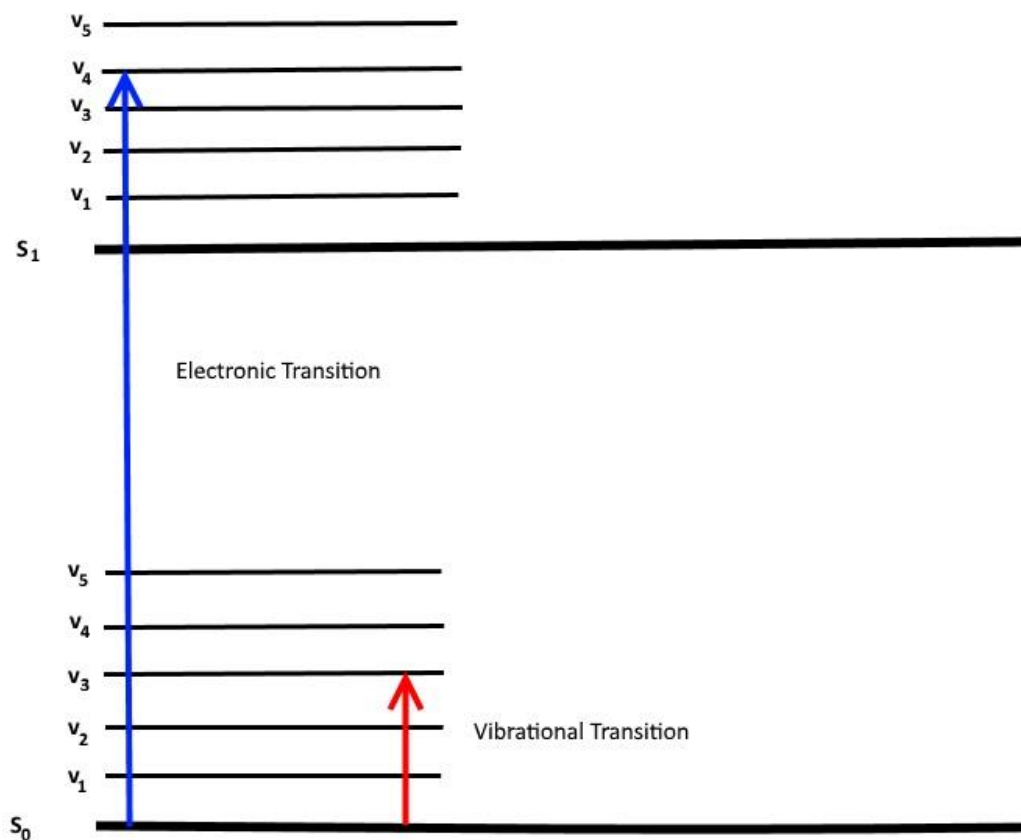

Figure 3: An energy level representation electronic and ro-vibrational transitions.

The light source used in this technique is a high power continuous-wave Optical

Parametric Oscillator (OPO). An OPO uses a 1064 nm Ytterbium doped fiber laser as a pump

and then splits the light into two separate beams. This results in three different laser beams, an

idler, signal, and pump being generated. The frequency of the pump beam is equal to the frequency of the idler plus the frequency of the signal. In the NICE-OHVMS, spectroscopy is accomplished mainly using the idler, with the pump and signal being sent to the optical frequency comb for high precision measurements. The optical frequency comb used in this experiment (Menlo FC1500) has been described previously but will be briefly explained here [1] [2] [3]. A frequency comb enables our measurements to have extremely high frequency precision on the order of MHz. The comb is used for stabilizing and measuring the pump frequency. It also measures the signal frequency after it has been shifted though a double-pass Acousto-Optic Modulator (AOM). This shifted frequency and the given AOM frequency are then differenced to calculate the unshifted signal frequency. When this unshifted signal frequency is subtracted from the stabilized pump frequency, a highly precise idler frequency is obtained.

The sample analyte is a positive column discharge. This positive column is created by first filling a triple-jacketed discharge cell, known as "Black Widow", with 100 mtorr – 2 torr of a gas mixture, and then ionizing the gas using two electrodes placed on either end of the cell. The gas is continuously flowed in and out of the cell so there is no noticeable pressure shift over the course of the experiment.

The detectors used in this experiment are a HgCdTe and InSb photovoltaic detectors. These detectors use semiconductors to convert the light transmitted through the sample to electricity, so the signal can be sent to a computer to be read in real time.

The absorption signals of ions are several orders of magnitude weaker than that of neutral molecules. This can be improved by using amplifiers with the detectors, but noise will also be amplified and the signal-to-noise ratio does not necessarily improve. A lock-in amplifier can be used instead to amplify these signals without amplifying the noise. A lock-in amplifier uses

phase-sensitive detection, which means that the signal is detected at a very narrow bandwidth, thus only amplifying the signal and not the noise. In order to achieve phase-sensitive detection, a frequency reference is required. A function generator is used to send an ~80 kHz square wave to the lock-in to be used as a reference. This reference is used to generate an internal reference for the lock-in amplifier. The lock-in multiplies this internal reference by the amplified signal using a phase-sensitive detector or multiplier. This can then be filtered to produce a clean DC signal proportional to the signal amplitude. The phase-sensitive detection plus low-pass filtration will only allow signals that have frequencies that are very close to the internal reference frequency be detected. Any noise signal that is far from the reference frequency is attenuated at the phase-sensitive detector by the low-pass filter. The bandwidth of the reference determines the bandwidth of detection. If the bandwidth of the filter is very narrow, the noise very close to the reference frequency will be removed, while a wider bandwidth will let this noise through [4]. The signal at the reference frequency is completely unaffected by the low-pass filter, which is good because that is the signal we want to measure.

To fully understand the NICE-OHVMS, it is important to understand how ion spectroscopy was done before. Over the past several years, instrumental advances have taken place to allow for new instrumental techniques to be developed. The next sections will describe the instrumental techniques that the McCall group used prior to the development of NICE-OHVMS to illustrate how the technique progressed over time.

Velocity Modulation Spectroscopy

The original workhorse of ion spectroscopy is known as Velocity Modulation Spectroscopy (VMS). VMS has become the most prominent method for discriminating between ionic absorption signals from neutral ones. A velocity modulated ion beam made by Wing et. al

was one of the initial experiments where VMS was put into practice [5]. The modern VMS experiment was described by Gudeman et al. in 1983 [6]. In VMS, two water-cooled electrodes are placed on the two ends of the discharge cell, Black Widow, and an alternating current is applied. This alternating current (AC) causes the polarity of the electrodes to switch at the modulation frequency (~ tens of kHz) such that one electrode is positive and the other is negative. As these electrodes continue to switch polarity at the given frequency, the positive ions created in the discharge will move towards the negative electrode and the neutral molecules stay still. This allows for detection of only positive ions generated in the discharge, completely ignoring the neutral molecules [7]. This is key in a positive column discharge experiment because the majority of molecules formed in the discharge are neutral molecules that will obstruct the absorption signals of the ions. VMS allows you to ignore any signal contribution that is a result of neutral molecules and solely detect ion signals.

In a traditional VMS experiment, the plasma is produced by an AC sine wave (~40 kHz) delivered to two water-cooled electrodes at the ends of the discharge cell. The plasma is generated by a step-up transformer, with the primary loop being driven by an audio amplifier (AE Techron 5050) in series with a 15 Ohm resistive load that stabilizes the plasma formation.

A typical VMS absorbance measurement of the R(1,0) transition for the molecular ion H_3^+ is shown in Figure 4. While this is the strongest transition of this particular ion, this level of signal-to-noise is not possible using traditional absorbance spectroscopy. The line shape for this VMS scan also looks different from that of a traditional absorption spectroscopy measurement. This is due to adding a layer of modulation to the traditional signal. Adding a layer of modulation allows for weaker signals to be detected and causes a pseudo-first-order derivative of the traditional absorption spectrum.
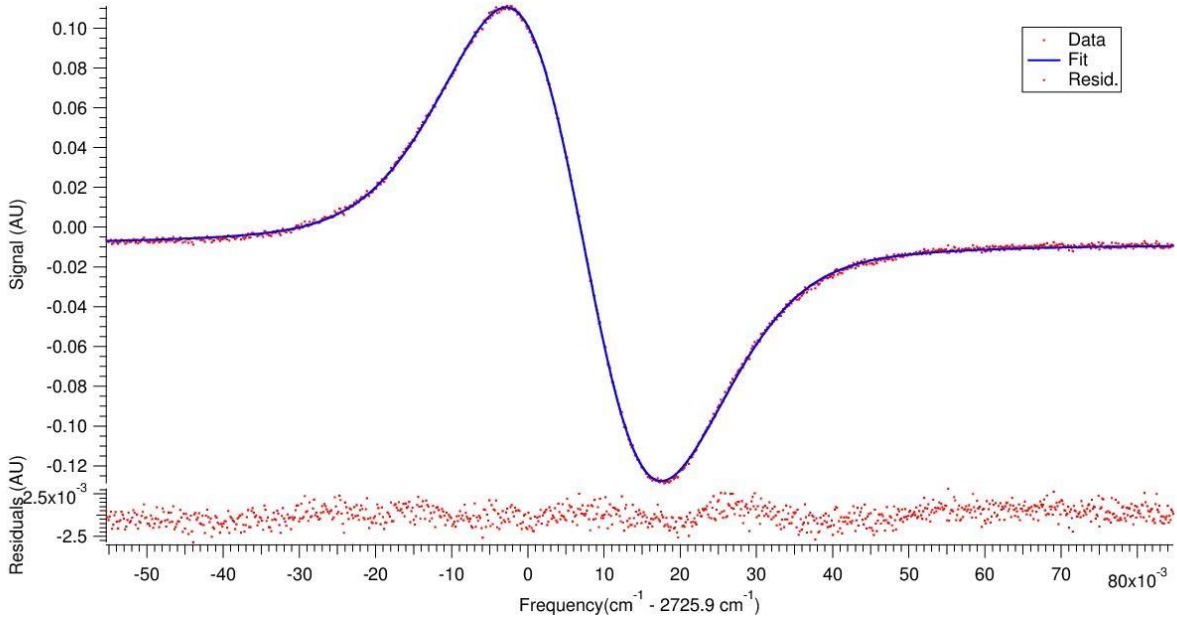
Figure 4: An example VMS scan of the R(1,0) transition of the H_3^+ ion (red dots top graph) with a fit to the data (blue line), and residuals of the fit (red dots bottom graph) [8].

Optical Heterodyne Velocity Modulation Spectroscopy

Pure VMS has its drawbacks, the most notable being the electrical pickup in the detection electronics and plasma light emission varying at certain discharge frequencies. This can be overcome by a combination of velocity modulation and frequency modulation spectroscopies, in a technique known as Optical Heterodyne Velocity Modulation Spectroscopy (OHVMS). OHVMS has been described previously and will only be described here briefly. For a more detailed description of OHVMS refer to Siller et al. [9]. With this technique, the same experimental set-up is used as with traditional VMS. The difference is that now the Ytterbium-doped fiber laser is frequency modulated (heterodyne) with a fiber-coupled Electro-Optic Modulator (EOM) using an RF generator at ~80 MHz for heterodyne detection. After the modulation is applied to this seed laser, it is amplified to 10 W total power using a fiber amplifier. This amplified beam is used as the pump for the OPO. From this point, the idler is sent

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though the positive column to the detectors and the pump and signal beams are sent to the frequency comb.

As it has been described by Siller et al., the OHVMS technique is a single-pass technique [9]. This means that the light source passes through the sample analyte exactly one time. This results in a line center shift that manifests as part of the velocity modulation. This can be corrected by either adding a numerical correction to the fit or by aligning two highly reflective spherical mirrors around the positive column. The addition of the mirrors allows for the light to pass through the cell and then be sent back and forth between the two mirrors. The number of passes through the cell can be adjusted with the alignment of the mirrors. At least two passes through the cell is necessary to eliminate the line center shift, as shown by Siller et al. [9]. The OHVMS technique is able to determine the line center of 20 transitions of HCO^+ with an average uncertainty of ~600 kHz [9]. This is significantly improved over both pure velocity modulation and traditional absorption spectroscopy.

An example of a scan and fit of the P(5) transition of HCO^+ using OHVMS is shown in Figure 5. While it is not very useful to compare the spectra of different molecules using different techniques, it is clear that there has been another enhancement of the signal-to-noise. The line shape for an OHVMS measurement is again different from a traditional absorption spectrum and also pure VMS. Now that there are two layers of modulation (frequency modulation and velocity modulation) the resulting line shape is similar to a pseudo-second-order derivative of the traditional absorption spectrum.
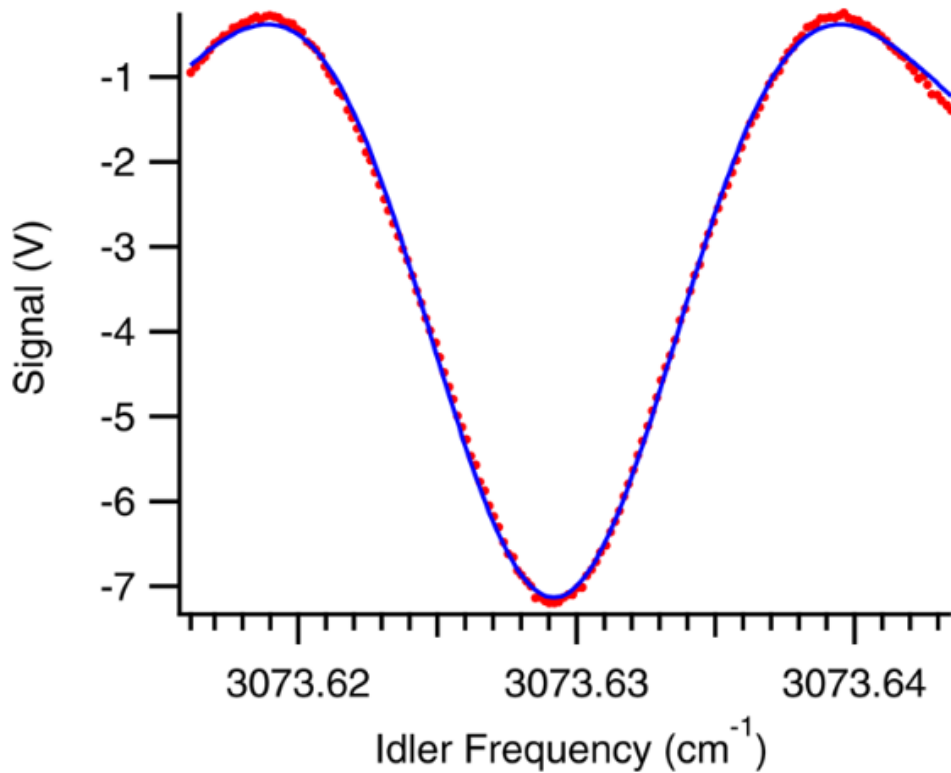
Figure 5: An example OHVMS scan of the P(5) transition of HCO+ (red dots) with a fit to the data (blue line) [9].

Cavity Enhanced Velocity Modulation Spectroscopy

An alternate approach to improve the limitations of pure velocity modulation spectroscopy is to place the positive column inside an optical cavity. This combination is known as Cavity Enhanced Velocity Modulation Spectroscopy (CEVMS). The addition of the optical cavity produces two major advantages; greatly increased path length and saturation creating sub-Doppler features, known as Lamb-dips [10]. The same type of spherical mirrors that would be used for multiple passes in OHVMS are used here to form the optical cavity. The formation of the optical cavity causes the laser to bounce back and forth between the mirrors hundreds of

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times. This simultaneously increases the effective path length of the laser path and saturates molecules due to the high intracavity power that is produced.

The plasma is produced in the exact same manner as a traditional VMS experiment, using an AC sine wave delivered to two water-electrodes and generated by a step-up transformer. The discharge cell is placed inside an optical cavity made using two fused silica dielectric mirrors. One mirror is mounted on a cylindrical piezoelectric transducer (Piezomechanik), which controls the length of the cavity [10]. The OPO is then locked to the cavity using the Pound-Drever-Hall (PDH) method [10].

The PDH locking method is very simple conceptually. The laser's frequency is sent through the optical cavity and measured, then the measurement is fed back to the laser to suppress frequency fluctuations that may arise. The measurement, or error signal, is made using a form of nulled lock-in detection that decouples the frequency measurement from the laser's intensity. This method allows for measurement and suppression of frequency fluctuations that occur faster than the cavity can respond. Therefore, the laser system is no longer limited by the response time of the cavity [11].

The back reflection from the cavity is sampled using a CaF_2 window and the sidebands are generated using an EOM. The output of the detector that monitors the back reflection is filtered before being mixed with the RF modulation frequency. This mixed output is filtered once more to produce the working error signal.

In Figure 6, a representative spectrum of a CEVMS scan is shown. In this scan, the red trace (a) corresponds to N_2^* and the blue trace (b) corresponds to N_2^+. The line shape is fairly similar to that of OHVMS because once again, there are two layers of modulation on top of the

traditional absorbance signal. The N_2^+ transition shows a line shape that corresponds to a pseudo-second-order derivative of a Gaussian, with a Lamb-dip shown in the center. This Lamb-dip is the result of the counter-propagating laser beams in the cavity. As the beams cross an ion, they effectively burn a spectral hole, resulting in the Lamb-dip shown in the blue trace (b) of Figure 6.
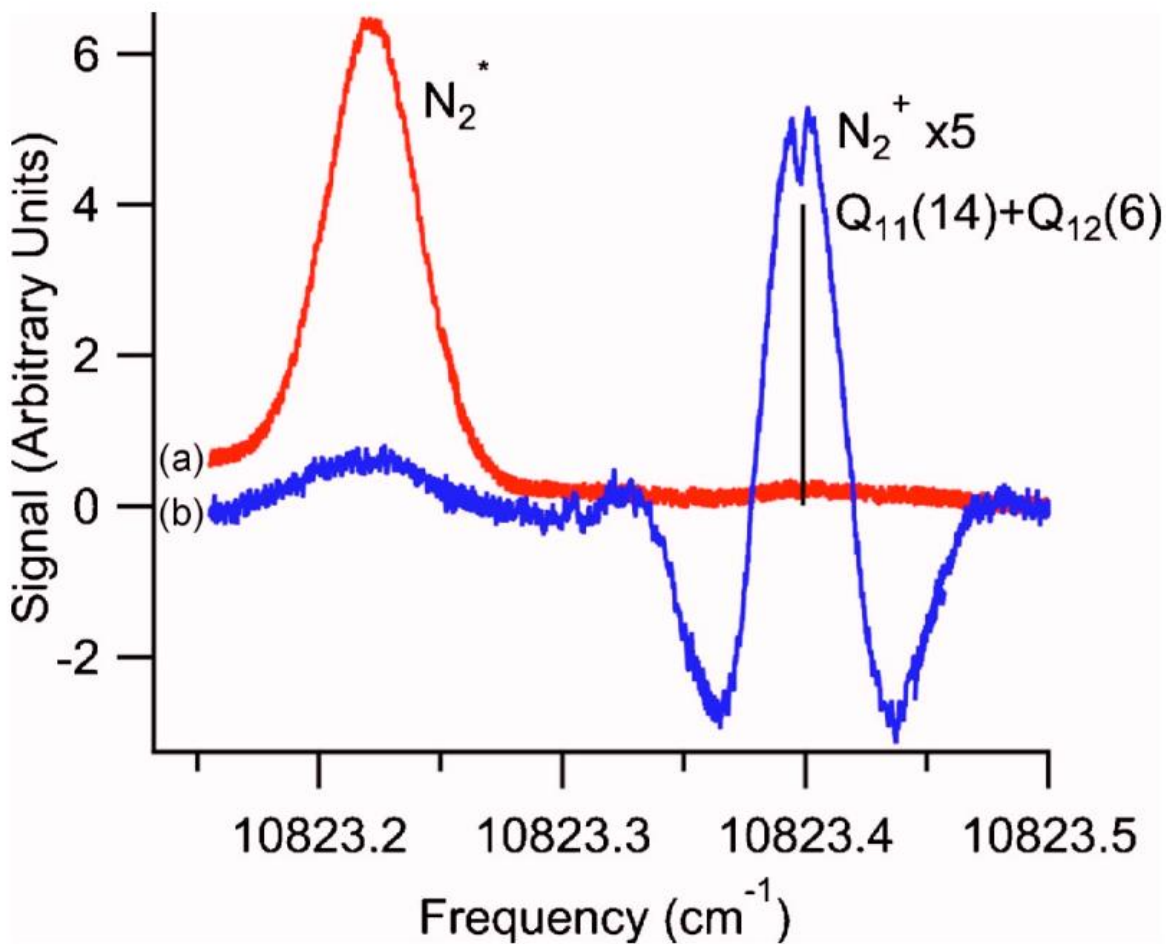

Figure 6: An example CEVMS spectrum of N_2^* (red trace, a) and N_2^+ (blue trace, b) [10].

Noise-Immune Cavity Enhanced Optical Heterodyne Velocity Modulation Spectroscopy

The NICE-OHVMS technique was inspired by the technique known as Noise-Immune Cavity Enhanced Optical Heterodyne Molecular Spectroscopy (NICE-OHMS). This technique was pioneered by Jun Ye in 1998, at JILA [12] [13]. The traditional NICE-OHMS experiment is essentially frequency (heterodyne) modulation spectroscopy that has been enhanced with an optical cavity. NICE-OHMS is an incredibly powerful technique that has the highest sensitivity of any instrumental technique to date. This technique combines an optical cavity with frequency modulation. The "noise immunity" of this technique comes from coupling the cavity with the frequency modulation to greatly reduce frequency noise that comes from the locking electronics [12] [13]. This is extremely powerful because with this technique, the quality of the lock no longer affects the quality of the spectrum or the accuracy of the measurements.

The technique Noise Immune Cavity Enhanced Optical Heterodyne Velocity Modulation Spectroscopy (NICE-OHVMS) can be thought of as adding velocity modulation to NICE-OHMS. The NICE-OHVMS technique was developed to utilize both the high precision of NICE-OHMS with the ion discrimination of VMS [1] [14]. The instrumental set-up is very similar to that of OHVMS; however, now an optical cavity is placed around the positive column, using high reflectivity (99%) dielectric mirrors. It can also be thought of as CEVMS experiment where the laser is now frequency modulated. A schematic representation of the instrument is shown in Figure 7.
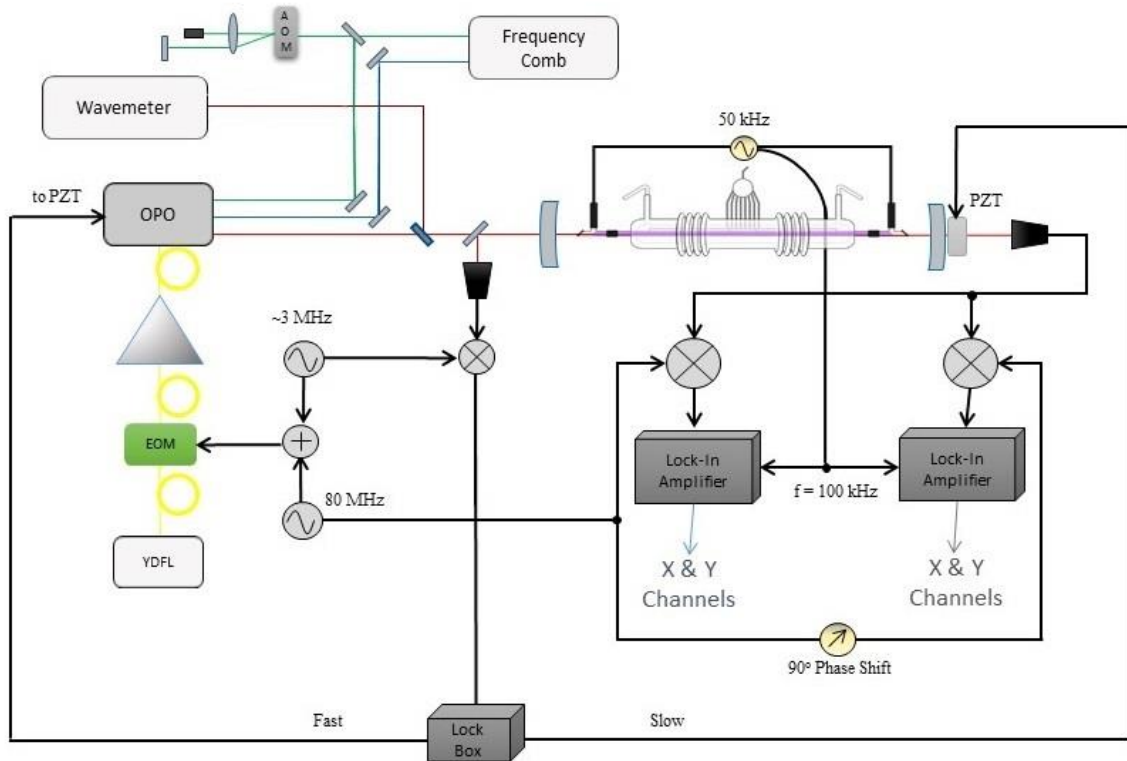
Figure 7: A box diagram of the experimental equipment in NICE-OHVMS.

The cavity and the idler are locked to maintain resonance using an InSb detector to monitor the back reflection of the front cavity mirror. The signal read by the InSb detector is demodulated with a mixer that is referenced to the PDH locking sideband frequency to generate an error signal. The output of the mixer is processed by a lock box and slow corrections (<100 Hz) are sent to a piezo on which one of the cavity mirrors is mounted in order to keep the cavity locked onto the idler at slow timescales. Faster corrections (0.1-10 kHz) are also sent to a piezo that controls the length of the OPO cavity, making small adjustments to the frequency of the signal and idler to keep the idler resonant with the external cavity on fast timescales. Based on the magnitude of this error signal, there is an extra ~500 kHz of random noise imposed on the

signal due to the locking of the idler to the external cavity. The idler radiation is coupled through Black Widow by two CaF_2 windows that are aligned at Brewster's angle. The transmitted light is detected and demodulated first at the heterodyne frequency of ~80 MHz by a pair of mixers that are 90 degrees out of phase with each other. The outputs of these mixers are further demodulated via lock-in amplifiers referenced to the heterodyne frequency, roughly twice that of the plasma frequency. This detection scheme results in four channels of detection: in-phase and quadrature detection for each of the two mixers; a schematic representation is shown in Figure 8.
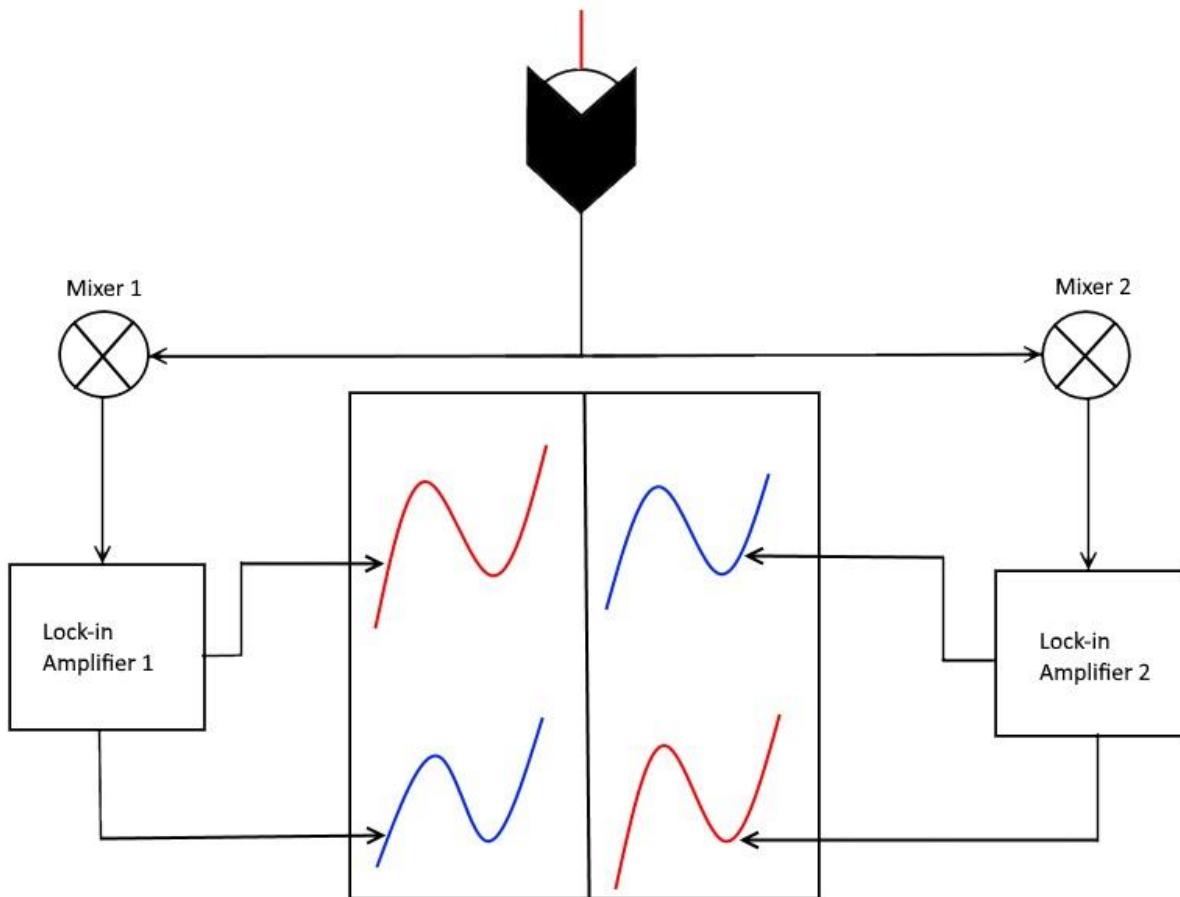

Figure 8: A schematic representation of the detection train that results in four channels of detection.

This ideally results in a separation of absorption and dispersion signals from each lock-in amplifier. This technique ultimately results in higher frequency accuracy in conjunction with the frequency comb because we are able to perform saturation spectroscopy. The saturated transitions result in sub-Doppler features known as Lamb-dips, which are located symmetrically around the zero-velocity component of the ions are not shifted by plasma asymmetries. Fitting to Lamb-dips eliminates any possible offset in line center frequency due to the AC plasmas used to generate ions.

The NICE-OHVMS technique has been used to study a variety of ions including, H_3^+, N_2^+, HCO^+, CH_5^+, HeH^+ and OH^+ [1] [2] [3] [14] [15]. Each of these molecular ions has had at least one transition saturated and then comb-calibrated to obtain the highest precision measurements to date. These values are in good agreement with older values and newer values from other research groups. An example scan for the R(1,0) transition of H_3^+ is shown in Figure 9. This scan shows great signal-to-noise and a well-defined Lamb-dip in the center. This is a scan of the strongest transition of H_3^+ so this can be considered a best-case scenario. The line shape of a NICE-OHVMS scan is once again different from the previous line shapes seen in the other experiments. There are now three layers of modulation on top of the traditional absorbance line, making the resulting line shape a pseudo-third-order derivative of a Gaussian.
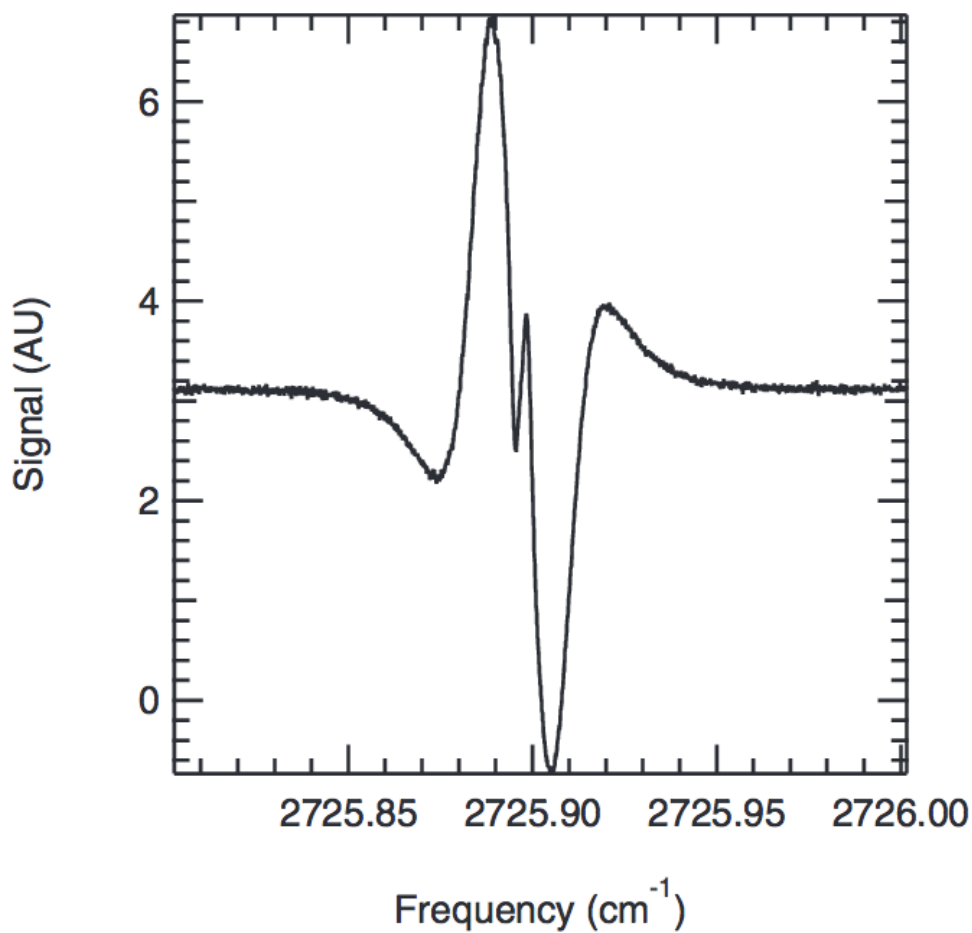
Figure 9: An example spectrum of the R(1,0) transition of H_3^+ with a Lamb-dip [1].

Part 2: Spectroscopy of the Deuterated Isotopologues of H_3^+

H_2D^+

The molecular ion H_3^+ has been studied for many years because of its fundamental importance to chemistry, physics, and astronomy. The McCall group has published several papers on H_3^+, all of which provide highly precise transitions to aid theorists in improving state-

of-the-art calculations [1] [15]. With H_3^+ being such an important molecular target for the McCall group, measuring highly precise values of its deuterated isotopologues is a logical next target. The deuterated isotopologues of H_3^+, H_2D^+, and D_2H^+ play key roles in deuterium fractionation of interstellar molecules [16]. Both of these isotopologues possess a permanent electric dipole that results in an allowed rotational spectrum that can be detected using radio telescopes [17]. It has also been shown that the ortho/para ratio of H_2D^+ is directly related to the ortho/para ratio of H_2 in dense cores [18].

The first measurements of H_2D^+ were made in 1981 by Shy et al. with no specific rotational assignments made at that time [19]. A tentative assignment of this spectrum was done by Carney and Porter, Carney, and Tennyson and Sutcliffe, where they performed exact ro-vibrational energy calculations for all deuterated isotopologues [20] [21] [22]. Amano and Watson measured and analyzed the ν_1 band in 1984, and shortly after Amano extended the calculations [16] [17]. The Oka group detected and analyzed the ν_2 and ν_3 bands of H_2D^+ in 1985 [18]. Most recently, the Schlemmer group has measured several transitions of H_2D^+ with a frequency comb, improving precision of values in the ν_1 band and several overtone transitions [23] [24]. Several groups have also measured transitions at 372 GHz and 156 GHz, with the 372 GHz emission line being used routinely for probing cold clouds [23].

H_2D^+ was attempted to be studied using the NICE-OHVMS technique, but unfortunately, there were several obstacles that prevented its measurement. The major factor that prevented its measurement was the coupling efficiency of the cavity where the ν_1 fundamental band of H_2D^+ is centered (2992.488 cm^{-1}). In this wavelength region, the cavity mirrors do not transmit light through the cavity as efficiently and as a result, the transmitted light can be a factor of two less than the optimal output. This decrease in transmitted light greatly affects the ability to lock the

cavity, as well as the ability to saturate molecular transitions. The coupling efficiency will never be perfect, that is 100% of the light will not be transmitted through the cavity even under the best conditions. However, it is possible to improve the coupling efficiency by removing the Brewster windows and connecting the cavity mirrors directly to the cell, a project that is currently ongoing. When this is accomplished, it should be possible to obtain highly precise measurements of the ν_1 fundamental band of H_2D^+.

D_2H^+

Similarly to H_2D^+, the other isotopologue, D_2H^+ plays a role in the deuterium fractionation of interstellar chemical reactions. Having a good understanding of fractionation processes will hopefully provide insight into the formation of the related deuterated species in space. D_2H^+ is a better target for our instrument because the ν_1 fundamental band is centered around 2736.997 cm^{-1}, where the coupling efficiency of our cavity is significantly better. The deuteration of H_3^+ is thought to be favorable because the isotopic exchange reactions:

$$H_3^+ + D_2 \rightarrow H_2D^+ + HD \tag{1}$$

$$\rightarrow D_2H^+ + H_2 \tag{2}$$

$$H_2D^+ + D_2 \rightarrow D_2H^+ + HD \tag{3}$$

$$\rightarrow D_3^+ + H_2 \tag{4}$$

$$D_2H^+ + D_2 \rightarrow D_3^+ + HD \tag{5}$$

are exothermic due to the differences in zero-point energies and the missing $J = 0$ level of H_3^+ [15].

Transitions in the ν_1 fundamental band of this species were first studied by Shy et al. using the Doppler-tuned fast-ion-beam, laser-spectroscopic method, with no definite assignments being made at that time [20]. Lubic and Amano later studied the ν_1 fundamental band while Foster, McKellar, and Watson measured the ν_2 and ν_3 band of D_2H^+ [25]. Recently, the first high precision measurements of D_2H^+ were made by Jusko and coworkers using LIR and a 4 K ion trap [27]. Amano and Hirao measured several submillimeter lines [28]. Amano later used these submillimeter lines as probes for chemistry in dark clouds [29]. This species has also been detected in cold prestellar cores by Parise and coworkers, which helped characterize the roots of deuterium chemistry [30].

A measurement of the $2_{02} \leftarrow 1_{11}$ transition of D_2H^+ (located at 2788.294 cm^{-1}) has been made using the NICE-OHVMS technique. Unlike H_3^+, D_2H^+ is an asymmetric top. This means that like water, D_2H^+ has an allowed rotational spectrum. The notation for these transitions is given by the principal quantum number J, as well as K_a and K_c, which are simply labels for an asymmetric top that refer to the prolate or oblate symmetric top limits. The mixing ratio of H_2:D_2 plays a large role in the intensity of the transition. A 1:1 ratio at 100 mtorr was used to achieve the strongest saturation, but raising the total 300 mtorr produced a larger Doppler profile with much smaller Lamb-dips. This trend follows what has previously been observed in other molecules studied using the NICE-OHVMS technique. An example scan of this transition is shown in Figure 10. This figure shows two of the four channels of detection where both channels have been saturated. This spectrum has only been wavemeter calibrated and is not a highly precise measurement of the line center. Unfortunately, due to time constraints a high precision measurement was unable to be obtained. However, this should be achievable in the future with minimal instrumental improvements.
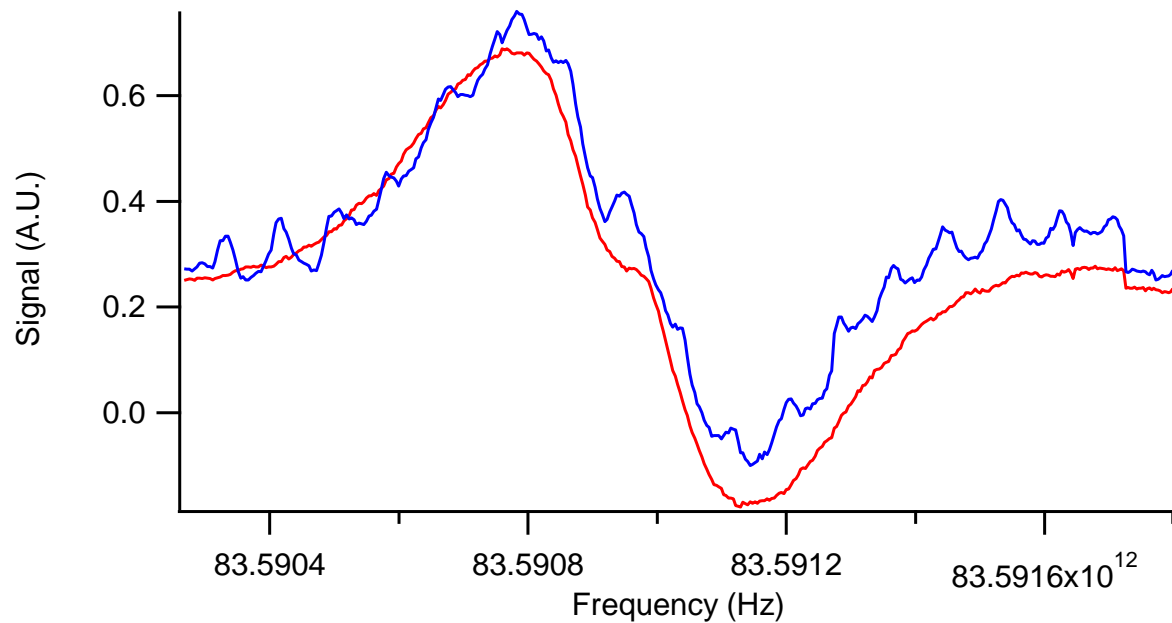
Figure 10: An example of a scan of the $2_{02} \leftarrow 1_{11}$ of D_2H^+ using NICE-OHVMS, displaying the in-phase and quadrature channels from one mixer.

This is the first deuterated species to be studied using NICE-OHVMS and the first transition of D_2H^+ to be saturated. An expanded survey of D_2H^+ lines can be accomplished in the future based on the work presented here.

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