Observation of the Infrared Saturation Spectrum of H_3^+ ν_2 Fundamental Band

Jow-Tsong Shy
Department of Physics
National Tsing Hua University
Hsinchu 30013, TAIWAN

Spectroscopy of v_2 fundamental Band

First observation by Oka in 1980

258 lines with J up to 14 observed by

1. Laser spectroscopy with positive column of glow discharge

Laser: DF (difference frequency generation) source

Lead-salt diode lasers

CC (color center) laser

2. FTIR spectroscopy with hollow cathode discharge

Absorption and emission spectrum

Doppler spectrum with accuracy is ~ 0.005 cm-1 (or 150 MHz)

Can one improve the accuracy?

New Developments ~ 2000

Optical frequency comb
→ improve wavelength accuracy

Periodically poled lithium niobate
→ improve laser power

Precision Doppler Spectroscopy Using PPLN DF Laser and Optical Frequency Comb

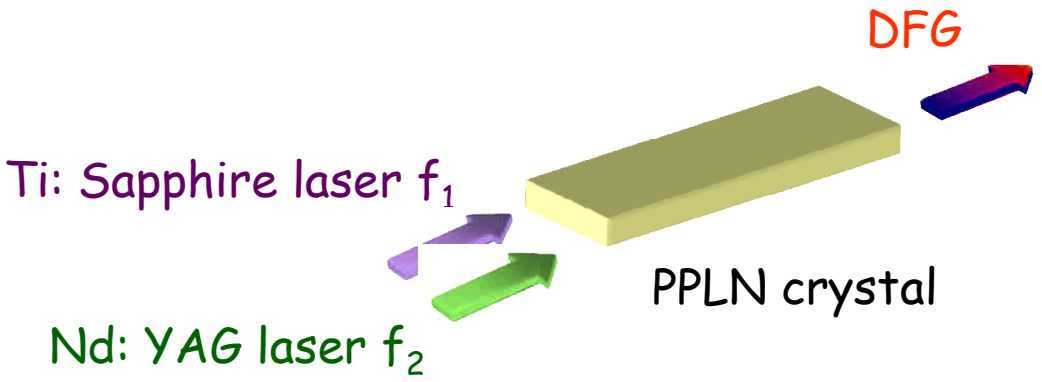
K.Y. Wu, C.C. Liao, and Y.H. Lien
National Tsing Hua University (Taiwan)

Optical Frequency Comb (OFC)

a "frequency ruler" for measuring unknown frequency in optical region

Femtosecond Mode-locked TiSa laser
(Giga Optics GigaJet 20)
Repetition Rate= 1 GHz
average power= 650 mW
covers the spectrum: 500 ~ 1100 nm
frequency accuracy : ~ 10^{-12} level

The mid-IR PPLN DFG source



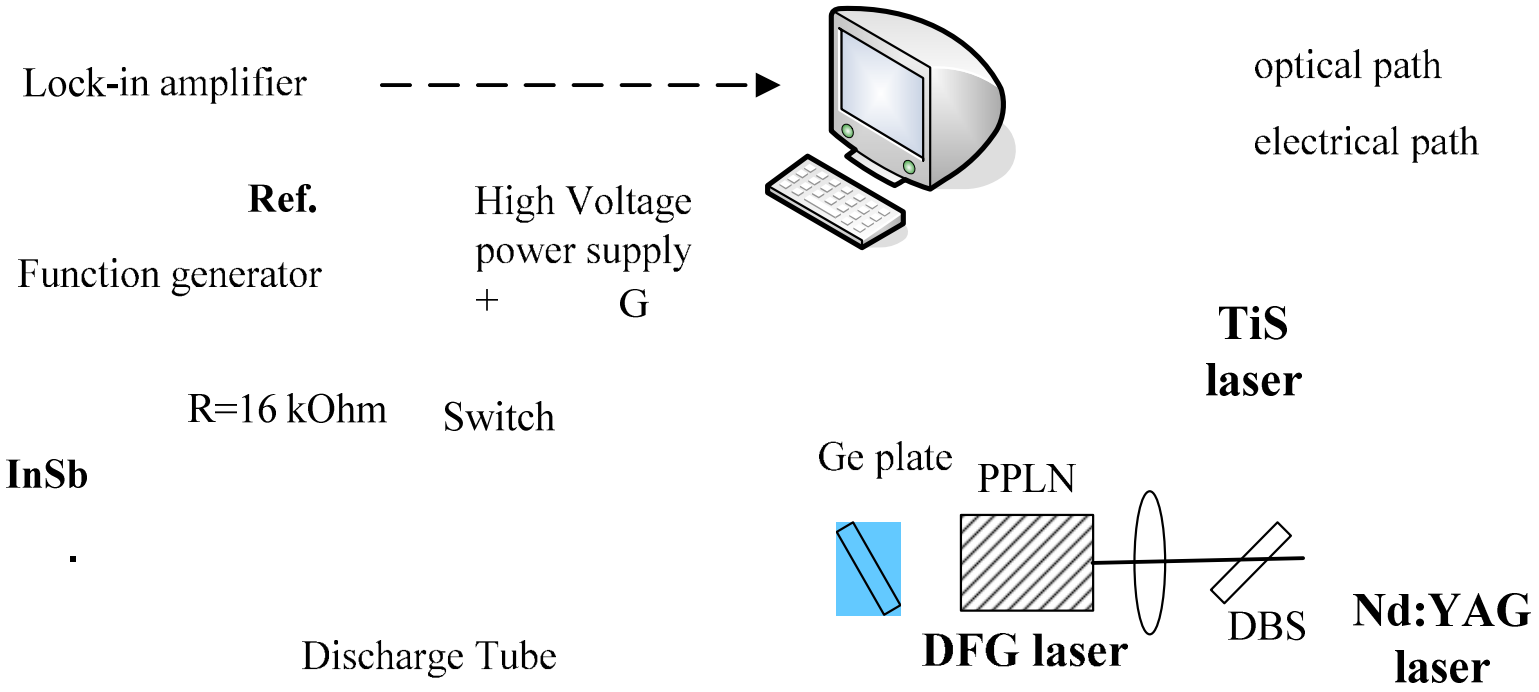
$$f_{DFG} = f_1 - f_2$$

Locked to a stable cavity

tunable

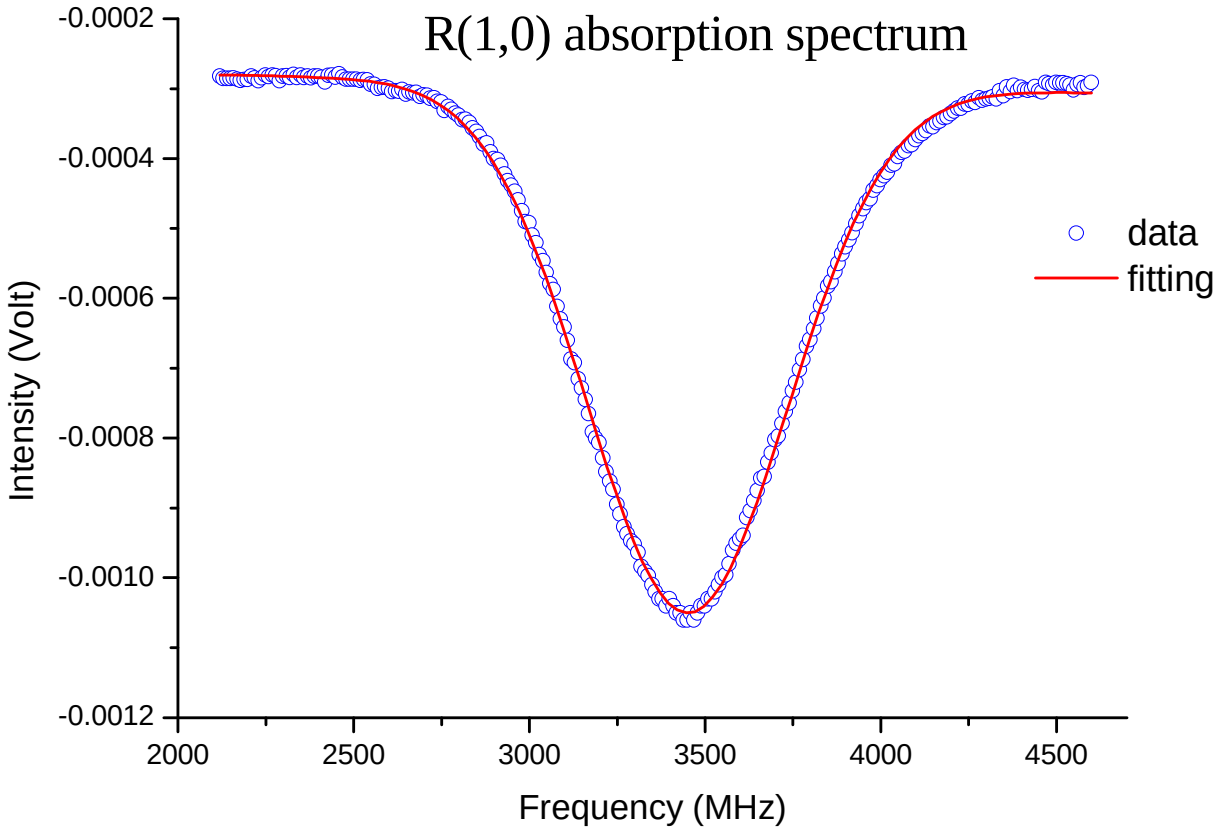
- Ti: Sapphire laser : $>$1.5 W at 780 ~ 870 nm
- Nd: YAG laser : ~1 W at 1064 nm
- Tunable over 2.92~4.77 μm
- ~ 1 mW at 3 μm
- $f_1$measured by our OFC and f_2 measured by an iodine-stabilized YAG laser

Experiment—concentration modulation



- H_2 pressure: 1.2 Torr
- methanol-cooled cell temperature : -25°C
- modulation frequency: 1.5 kHz

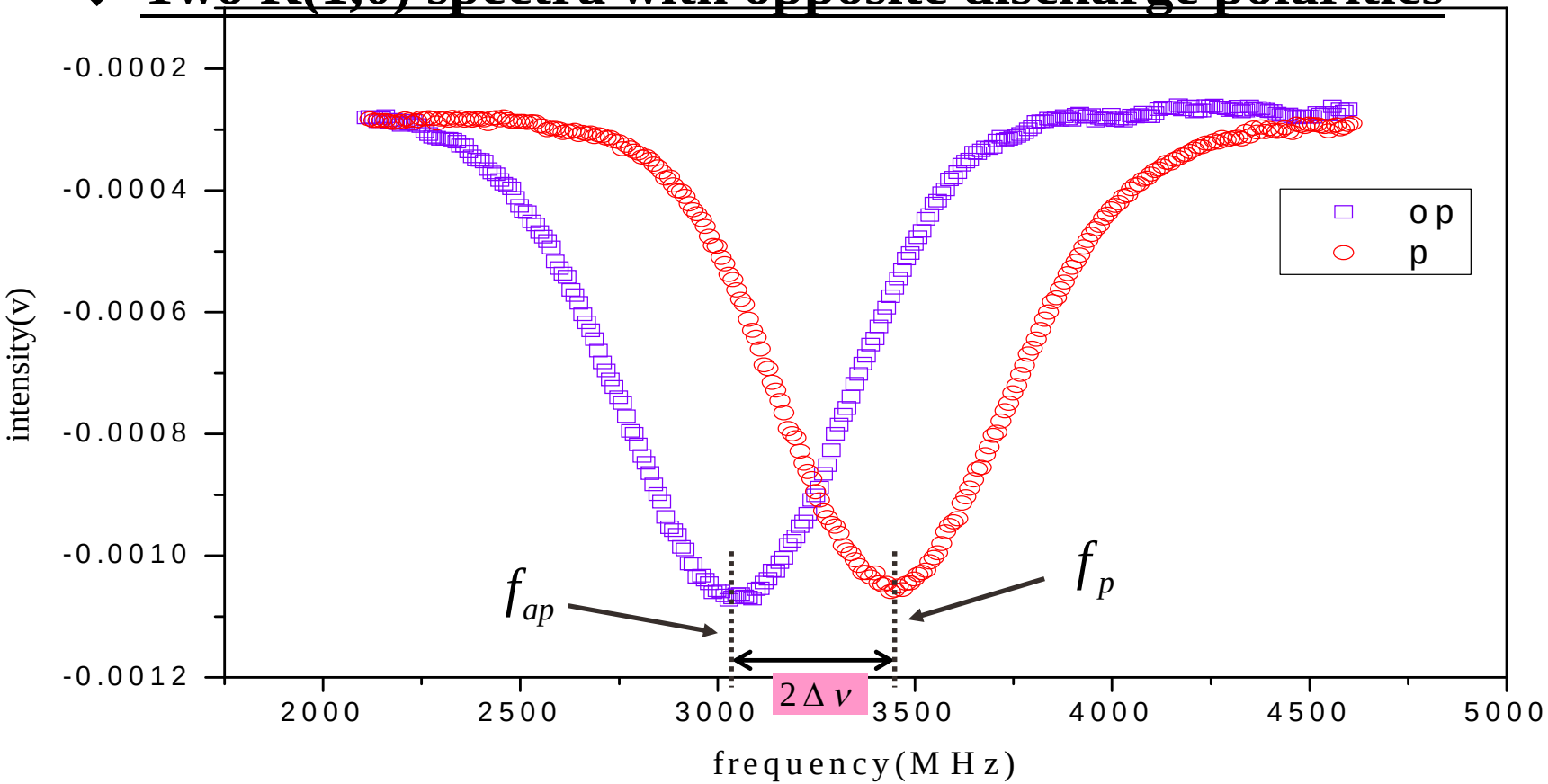
Doppler spectrum



- fitting uncertainty of central frequency < 1 MHz
- Doppler linewidth ~ 578 MHz (~ 300 K)
- Sensitivity ~ 1×10^{-8} $cm^{-1}Hz^{-1/2}$

Frequency measurements

◆ **Two R(1,0) spectra with opposite discharge polarities**



The transition frequency is determined by $f_0 = \dfrac{f_{ap} + f_p}{2}$

Results

transitions	Our results (cm^{-1})	uncertainty	other groups (cm^{-1})	uncertainty
$R(3,3)^u$	2918.02561(35)	10 MHz	2918.026(10) [1]	300 MHz
$R(3,3)^l$	2829.92527(35)	10 MHz	2829.925(05) [2]	150 MHz
$R(2,1)^u$	2826.11683(35)	10 MHz	2826.117(05) [2]	150 MHz
$R(2,2)^u$	2823.13780(35)	10 MHz	2823.138(05) [2]	150 MHz
$R(2,2)^l$	2726.06965(35)	10 MHz	2762.070(05) [2]	150 MHz
$R(1,1)^u$	2726.22025(35)	10 MHz	2726.220(05) [2]	150 MHz
$R(1,0)$	2725.89816(35)	10 MHz	2725.898(05) [2]	150 MHz
$R(1,1)^l$	2691.44305(35)	10 MHz	2691.443(05) [2]	150 MHz
$Q(2,2)$	2554.66586(70)	20 MHz	2554.666(05) [2]	150 MHz
$Q(1,1)$	2545.42036(70)	20 MHz	2545.420(05) [2]	150 MHz
$Q(1,0)$	2529.72464(35)	10 MHz	2529.724(05) [2]	150 MHz
$Q(2,1)^l$	2518.21154(70)	20 MHz	2518.211(05) [2]	150 MHz

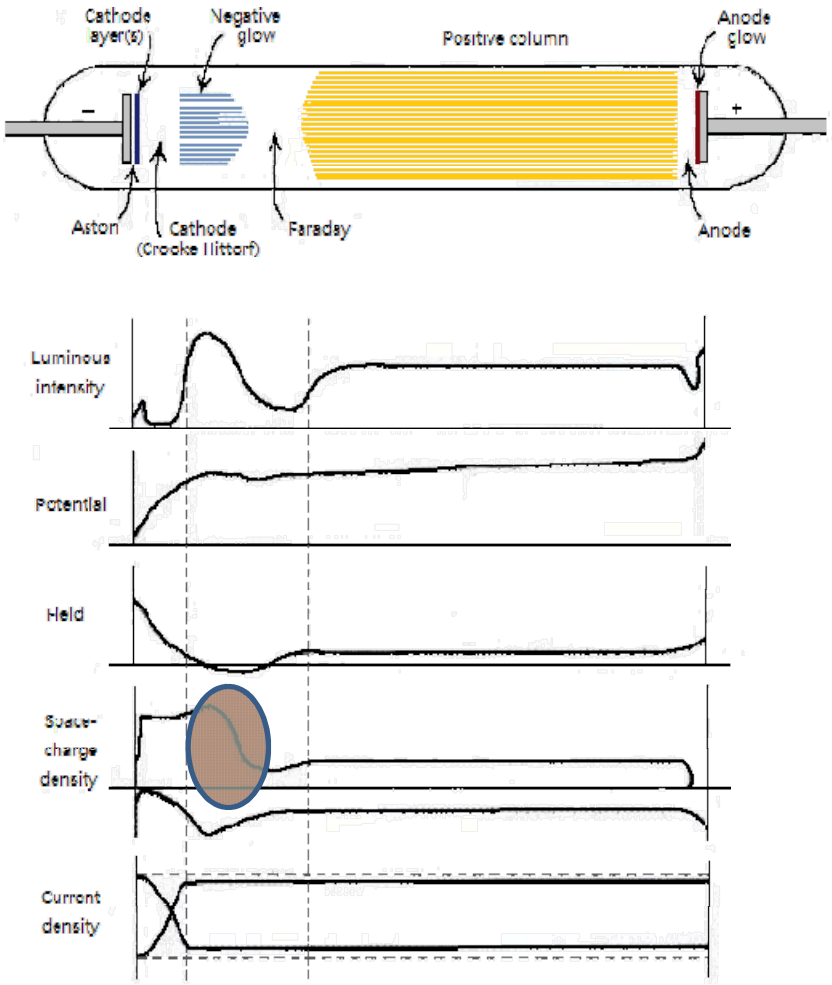
[1] T. Oka, *Phil. Trans. R. Soc. Lond. A* 303,545-549 (1981).

[2] A. R. W. McKellar and J. K. G. Watson, *J. Mol. Spectrosc.* 191, 215-217 (1998).

The uncertainty of previous results is ~ 0.001 cm^{-1} (30 MHz)

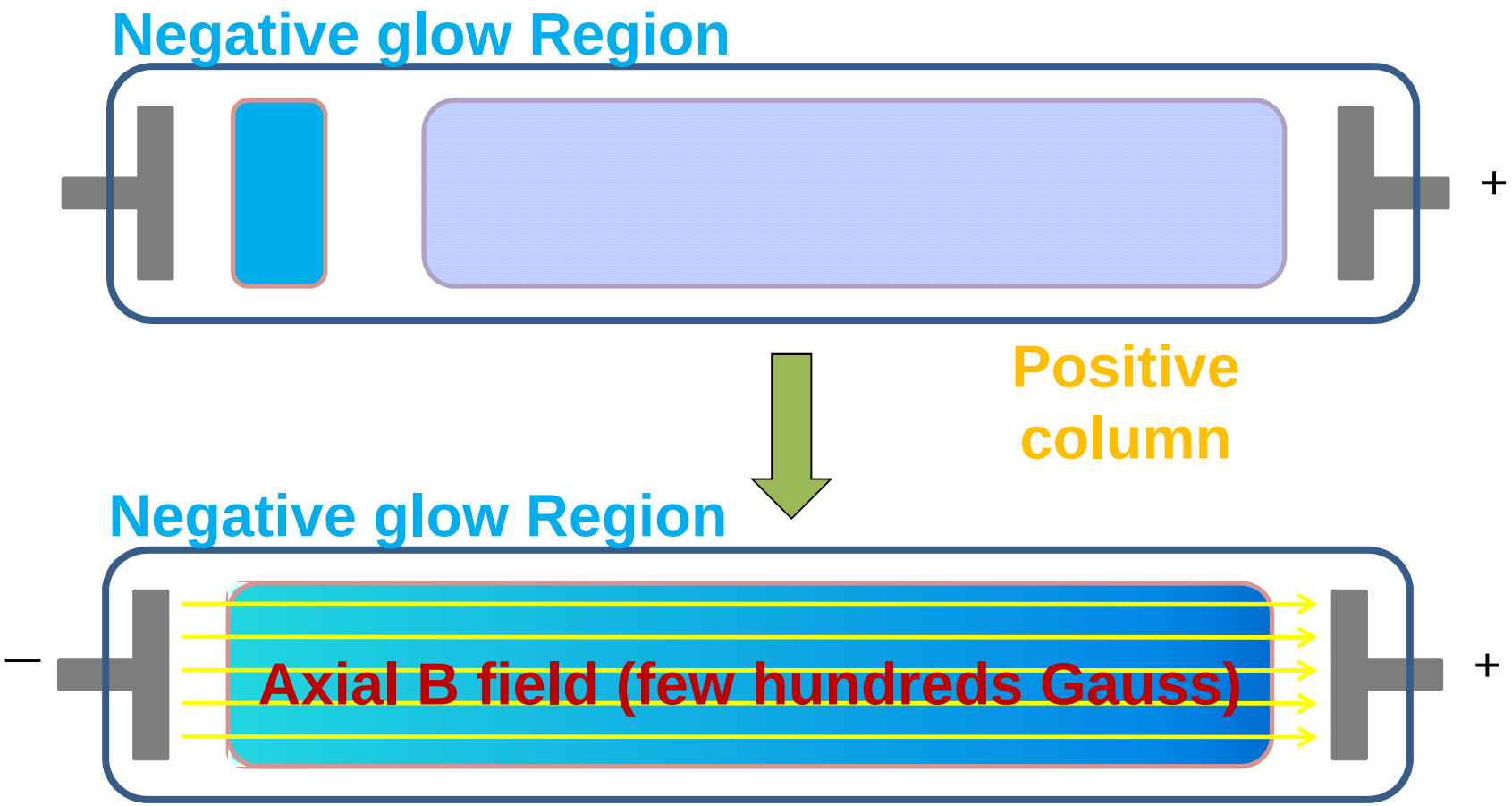
Saturation spectrum of H_3^+

Direct-Current Glow Discharge



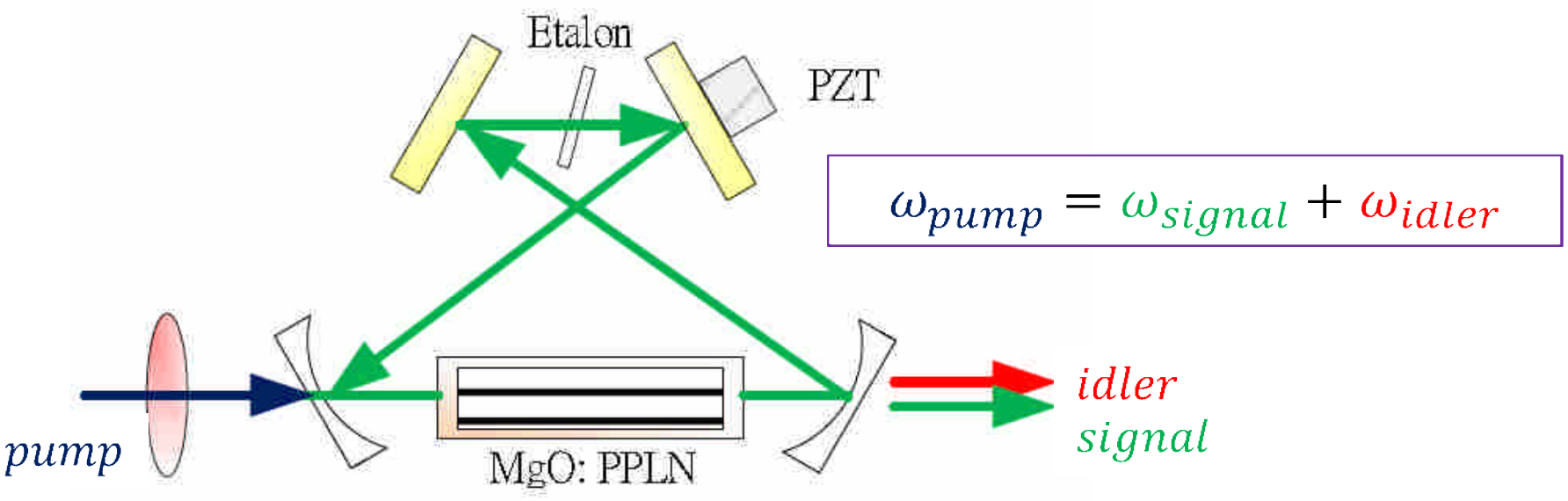
- **The region is relatively short**

Extended Negative Glow Discharge



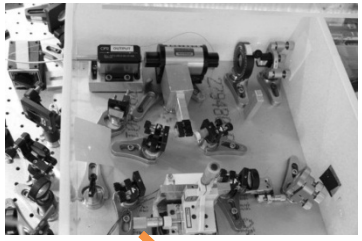
High ion concentration at low pressure.

Singly Resonant OPO

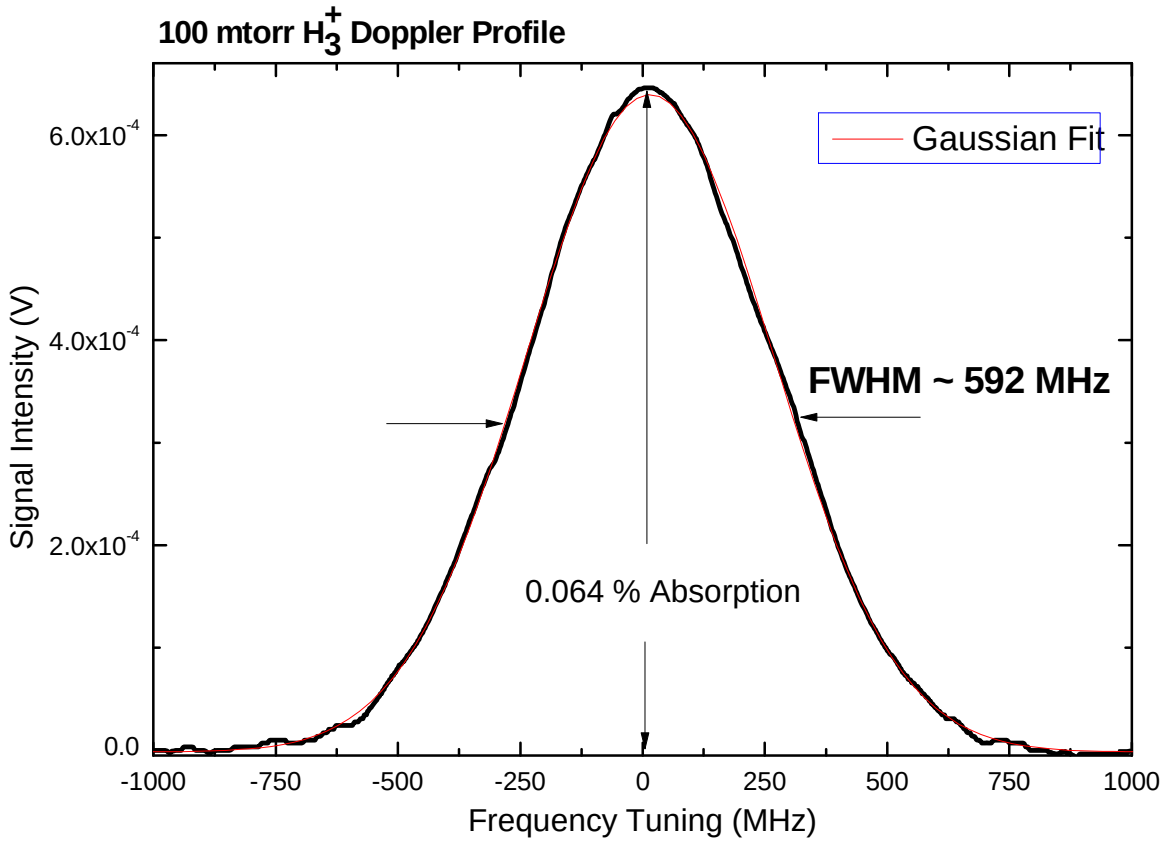


- Increasing the signal of the saturation spectroscopy of molecular ion.
- Idler Wavelength :**2.7 – 3.9 µm**
- Average Power : > **300 mW**

Experimental Setup

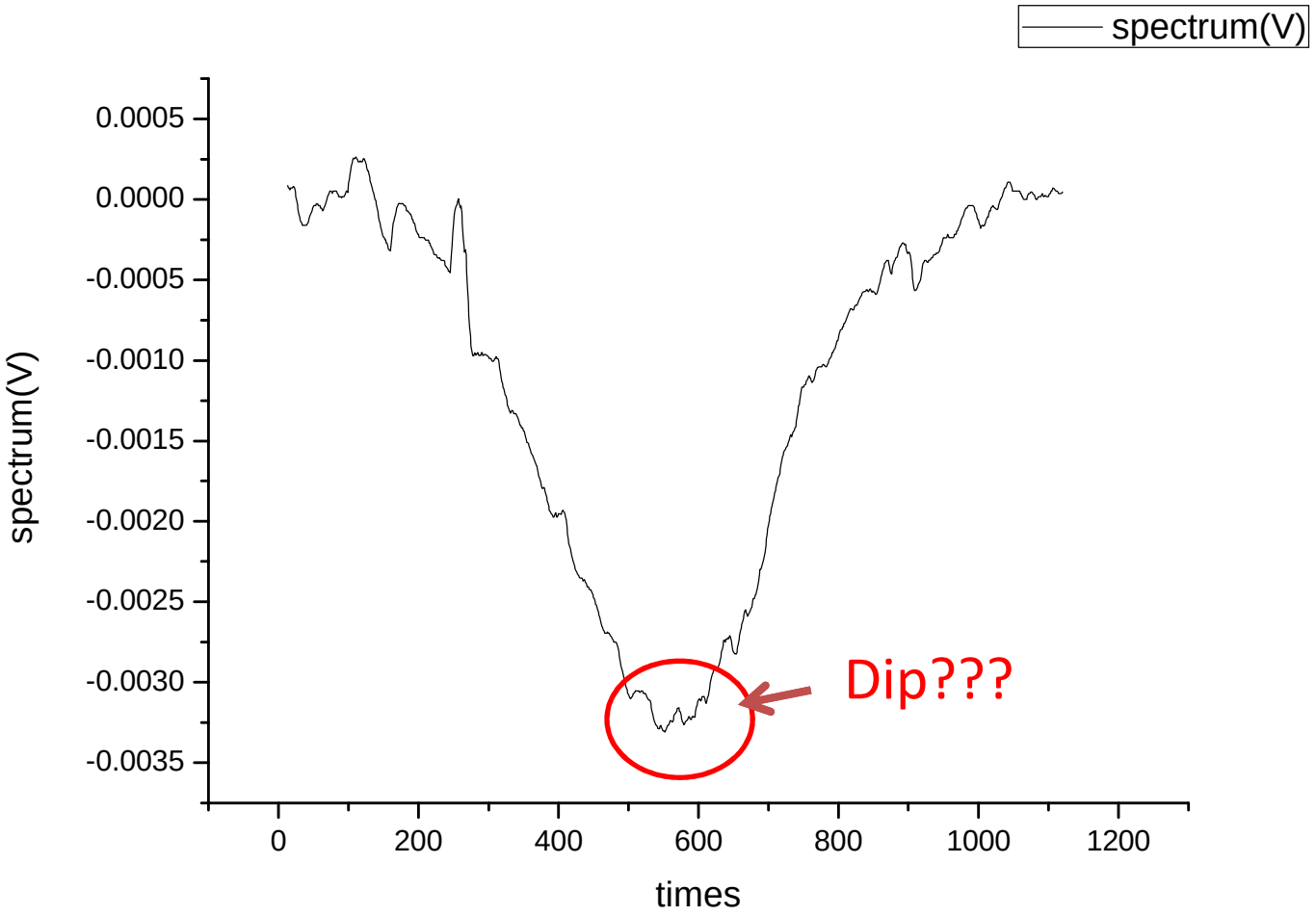


Absorption of R(1,0)

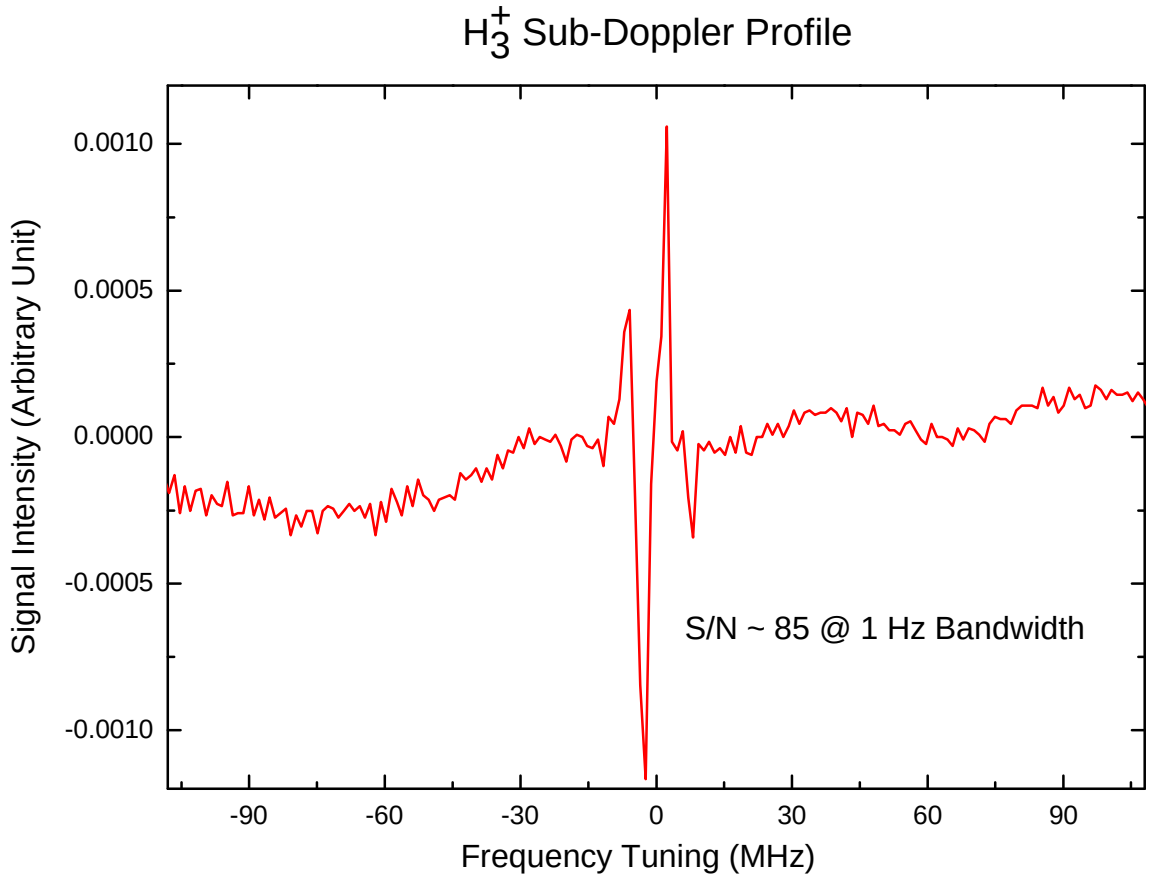


- B Field Modulation -- Concentration Modulation
- Doppler width (FWHM): 590 MHz (~ 300 K)
- Absorption: 0.036 %

Increase OPO Power



3rd Derivative Signal - Saturation Dip



- Frequency Modulation Method – Idler wave
- Modulation Frequency : 31 kHz
- Modulation Depth : 28 MHz
- Laser Intensity : ~ 80 kW/m^2

Fiber Optical Frequency Comb

- Repetition Rate : 250 MHz
- Supercontinuum : 1030 ~ 2200 nm
- Accuracy : < 10^{-12} @ 1000 sec (< 1 kHz in the MIR region)

Frequency determination

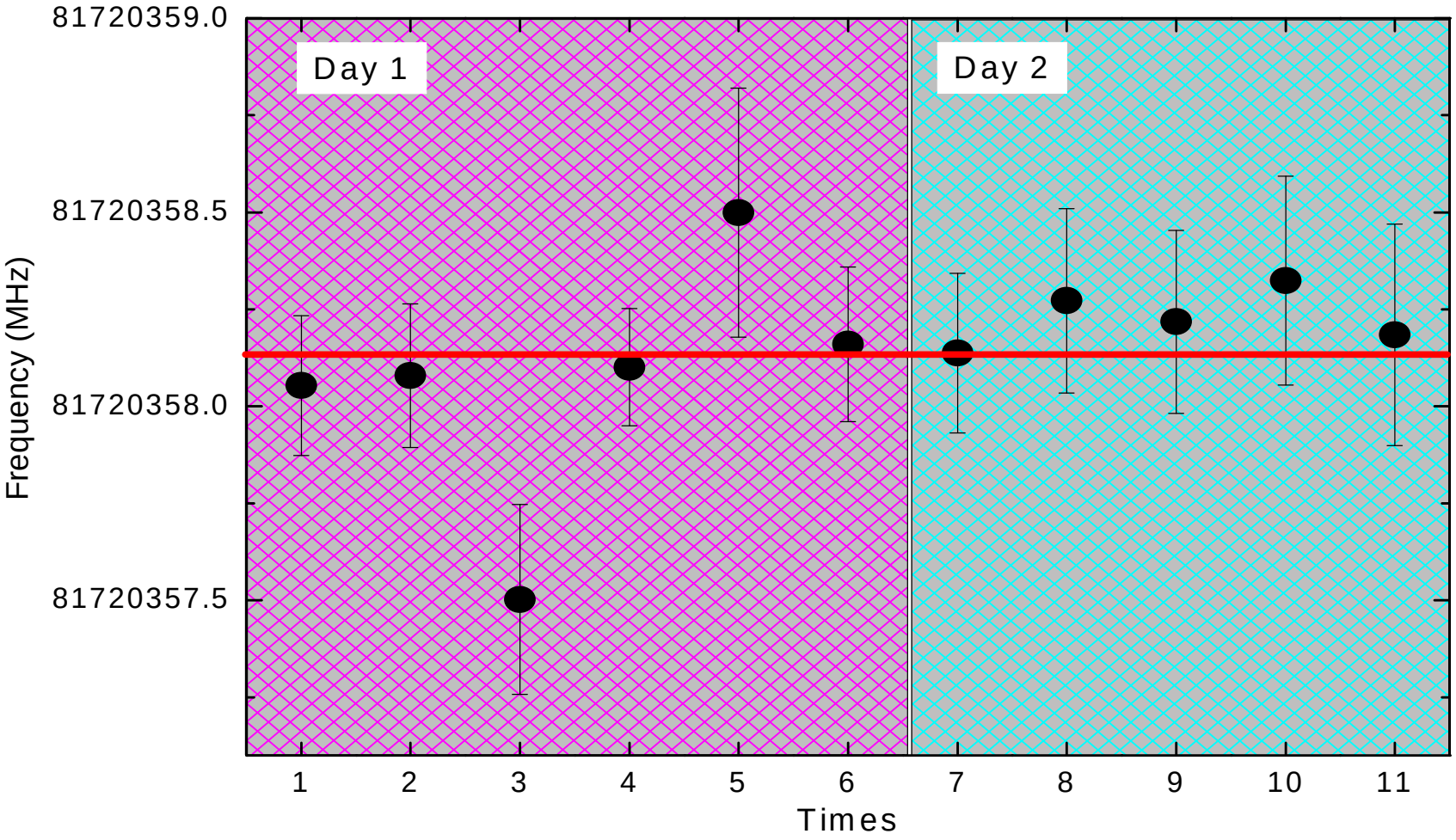
1. Lock signal to comb, 2. Lock pump to line center, and 3. Measure pump frequency with frequency comb

1.062 μm 1.4-1.8 μm 2.7-3.9 μm

$$\omega_{pump} = \omega_{signal} + \omega_{idler}$$

$$f = n \cdot f_{rep} \pm f_{b,pump} \pm f_{b,signal}$$

Frequency Measurement H_3^+ R(1,0)



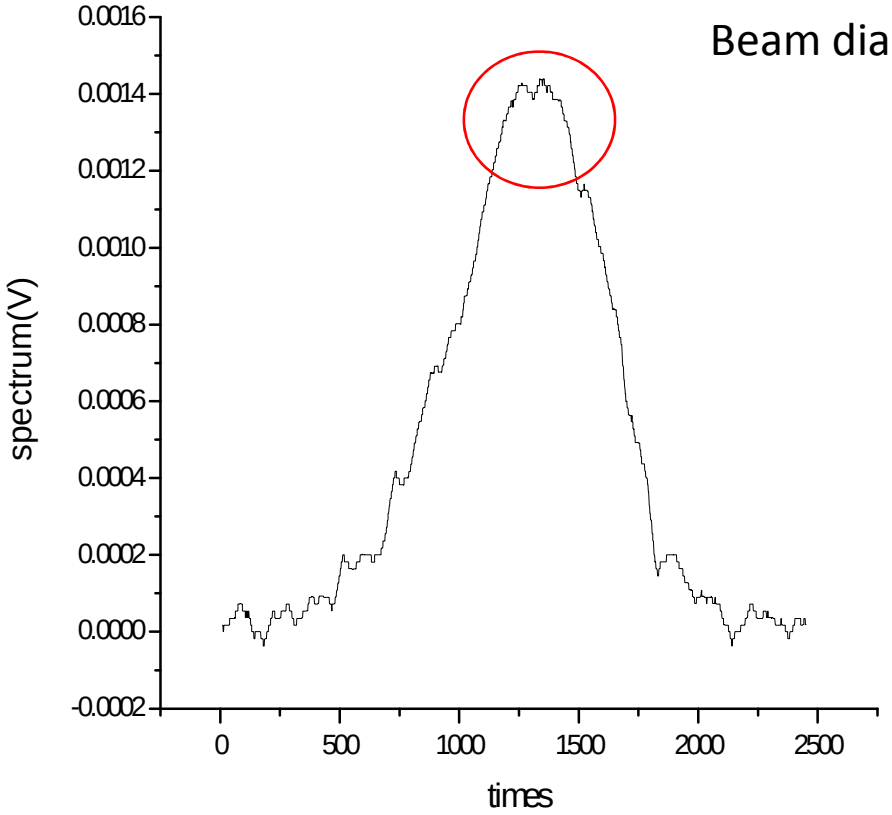
Our Measurement: 2725. 897 732 2 (26) cm^{-1} (81720 358 138 (78) kHz)

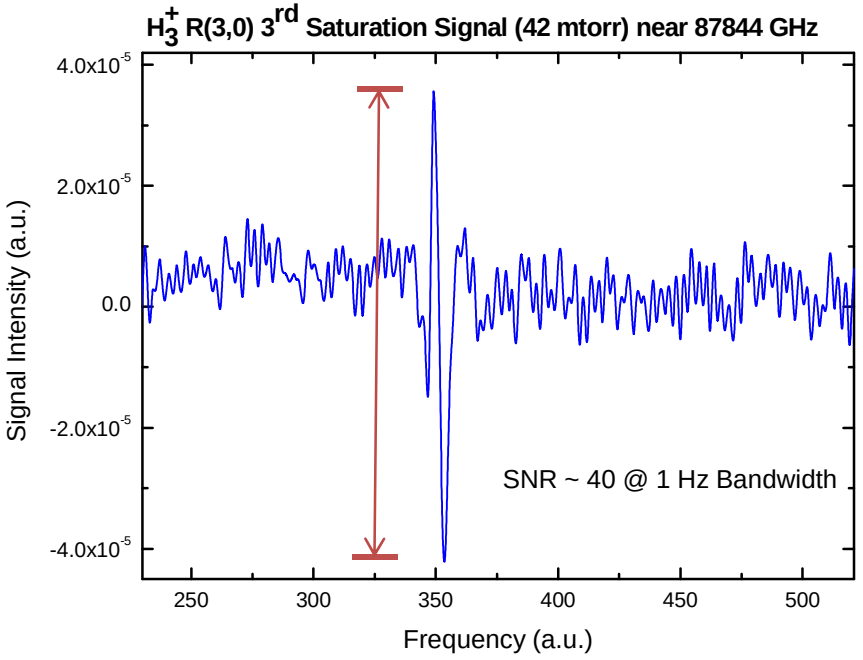
Previous Measurement: 2725.898 (5) cm^{-1}

Agree very well, but much higher accuracy!

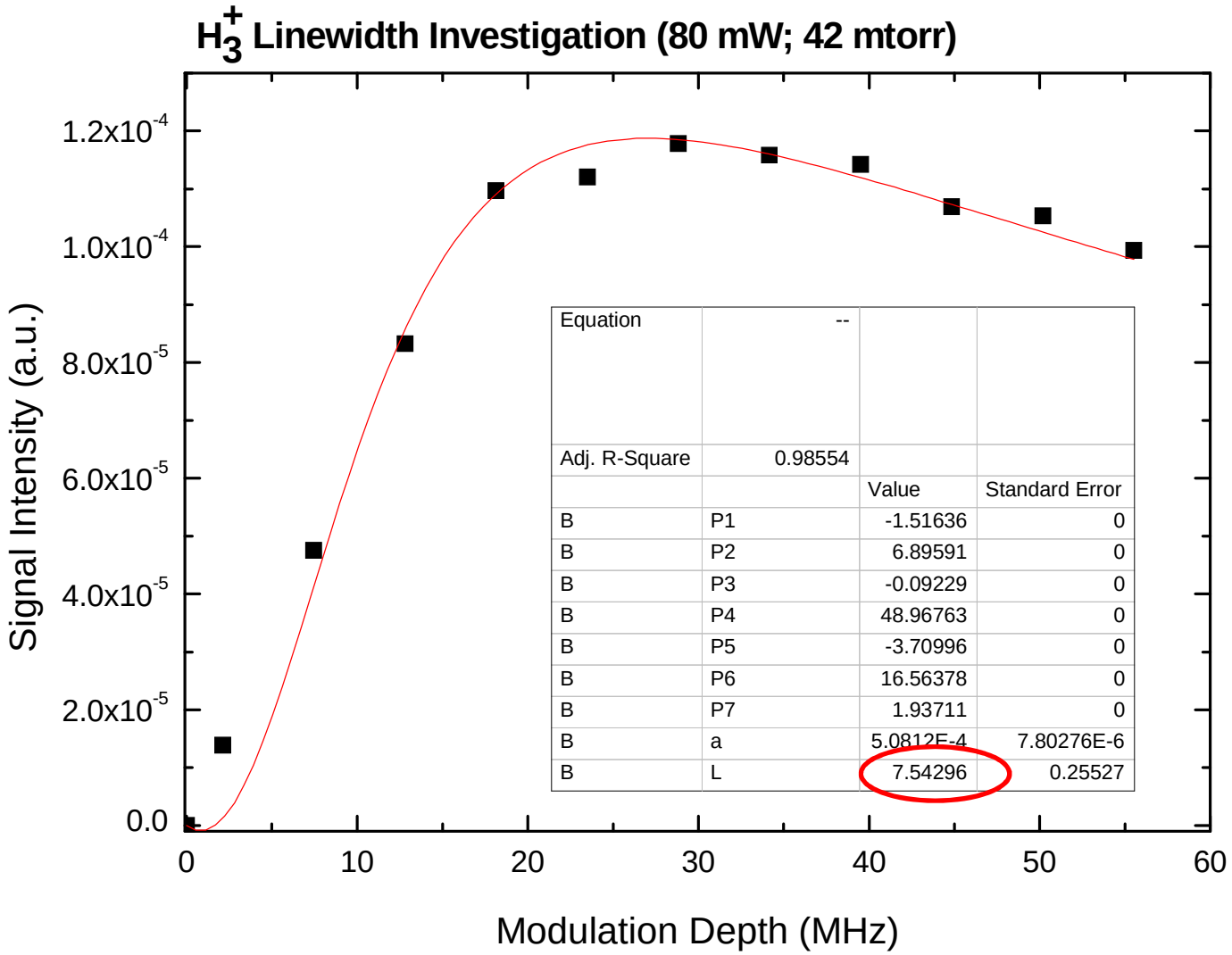
H_3^+ R(3,0) @ 3.412 μm

Pressure 60 mtorr
Power 100 mW
Beam dia 1.23 mm

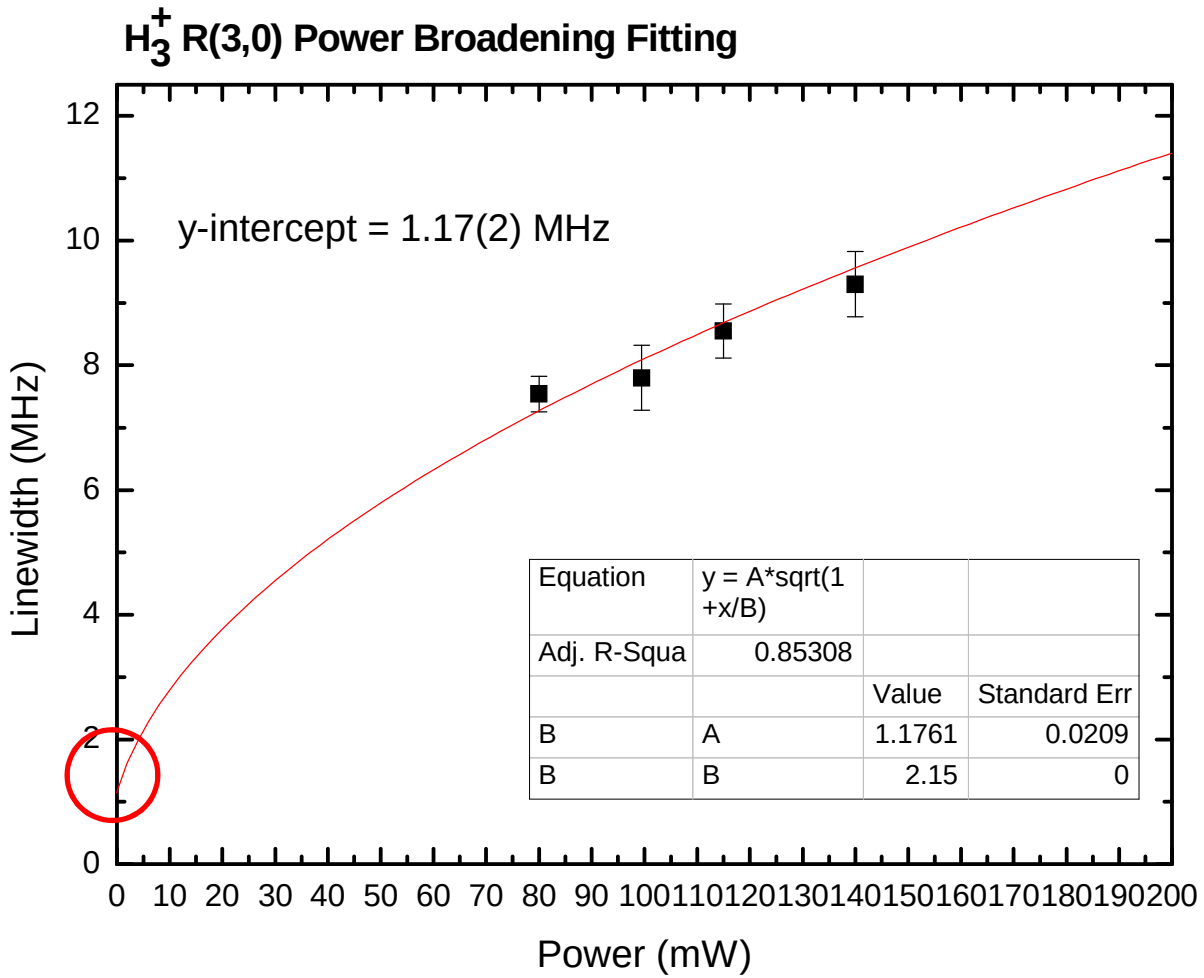




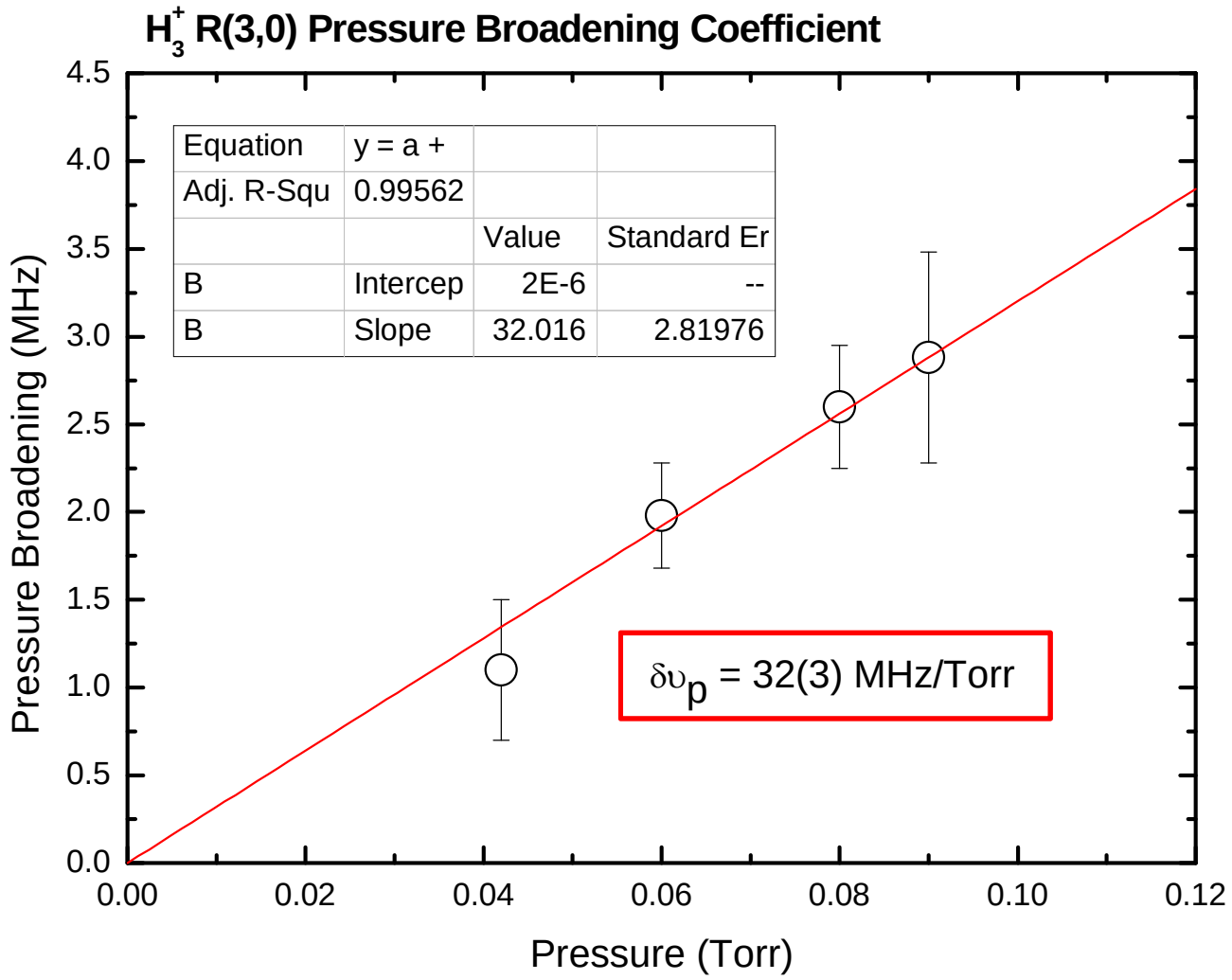
Linewidth at 80 mW 42 mtorr



Pressure Broadened Linewidth (42 mtorr)



Pressure Broadening Coefficient



See our poster for the details.

Conclusions

- **First observation of the saturation spectrum of H_3^+ in an extended negative glow discharge using a PPLN OPO**
- **The absolute frequency of H_3^+ R(1,0) transition has been determined to high accuracy (< 100 kHz).**
- **The power and pressure broadening of R(3,0) transition has been studied.**

Future Works

- **Improving the sensitivity of our spectroscopic system.**
- **Measuring other transitions of H_3^+.**
- **Study other molecular ions: HeH^+, H_3O^+,…**
- **Calibrate the accuracy of velocity modulation spectroscopy**

Acknowledgments

$$: NSC, MOE, and ITRI (Taiwan), NSERC (Canada)