FAR-INFRARED SPECTROSCOPY OF SHORT-LIVED SPECIES

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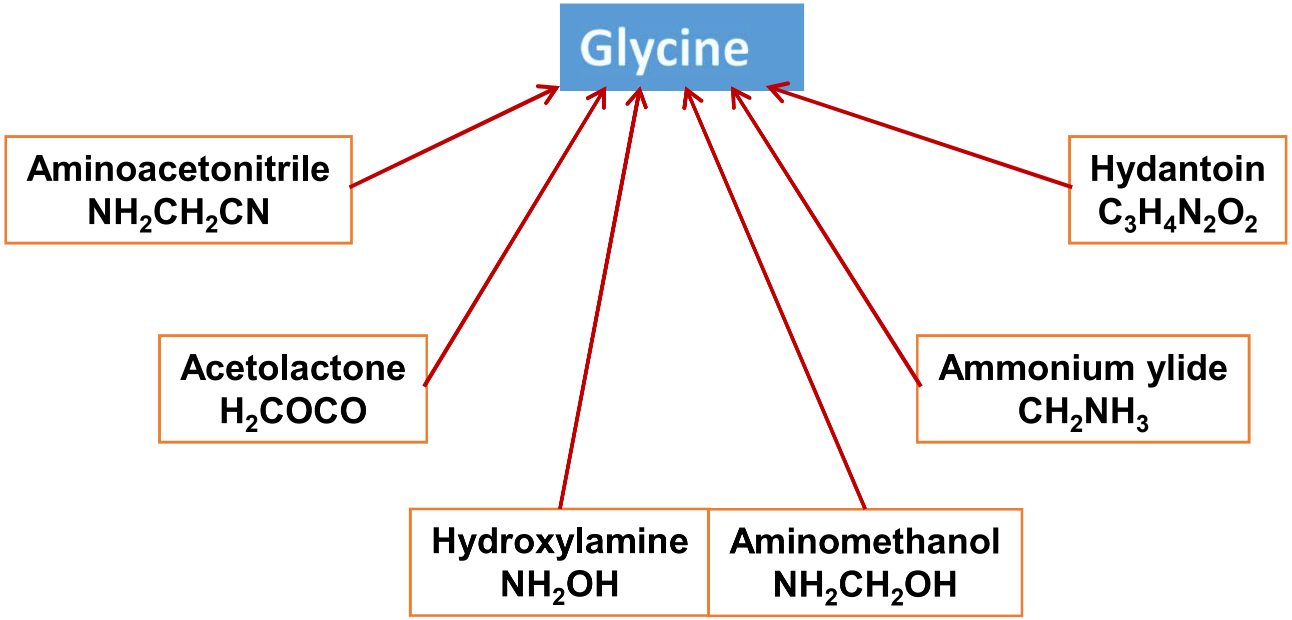
RI05 73rd ISMS mini-Symposium Far-Infrared Spectroscopy

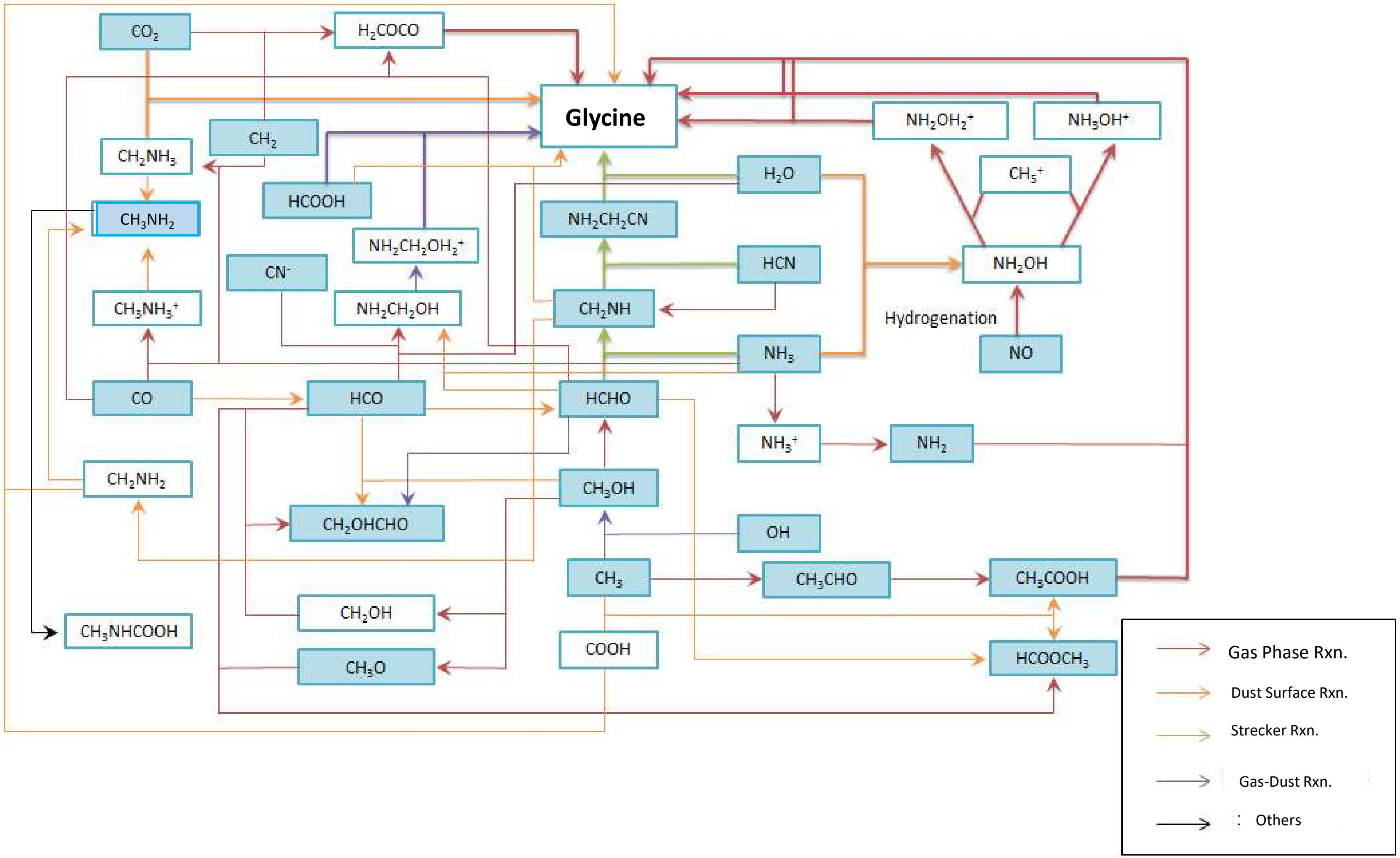
Contents

- Spectroscopy of radicals
  - Motivation
  - “Some” keys for spectroscopy of radicals
- 3 examples
  - Methylene (CD_2)
  - Amidogen (NHD)
  - Di-fluoromethyl (CHF_2)

Possible precursors of Glycine



Road to Glycine

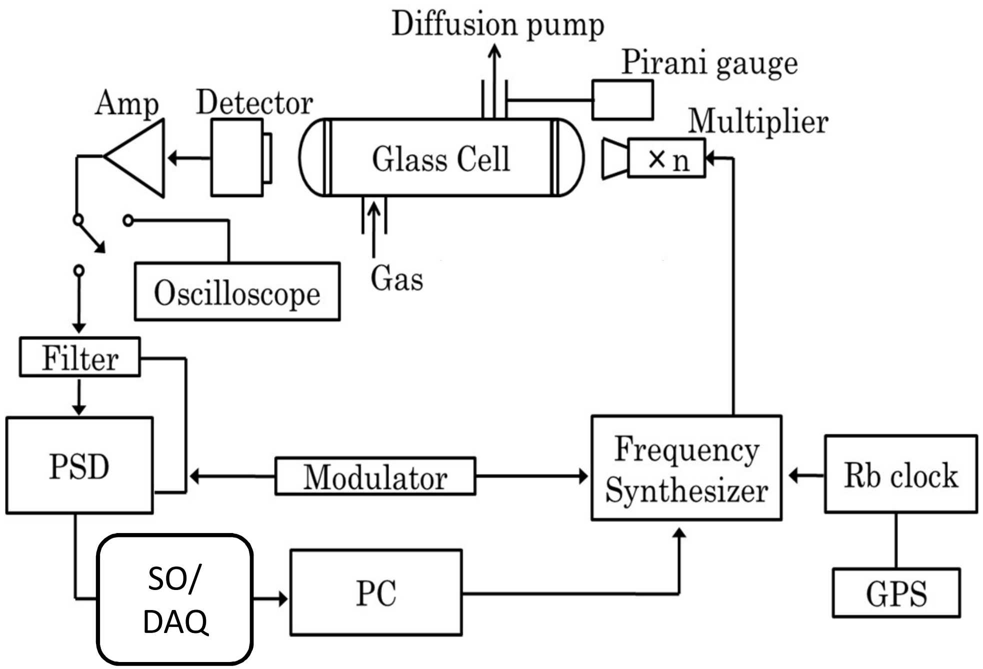


Keys for spectroscopy of short-lived species

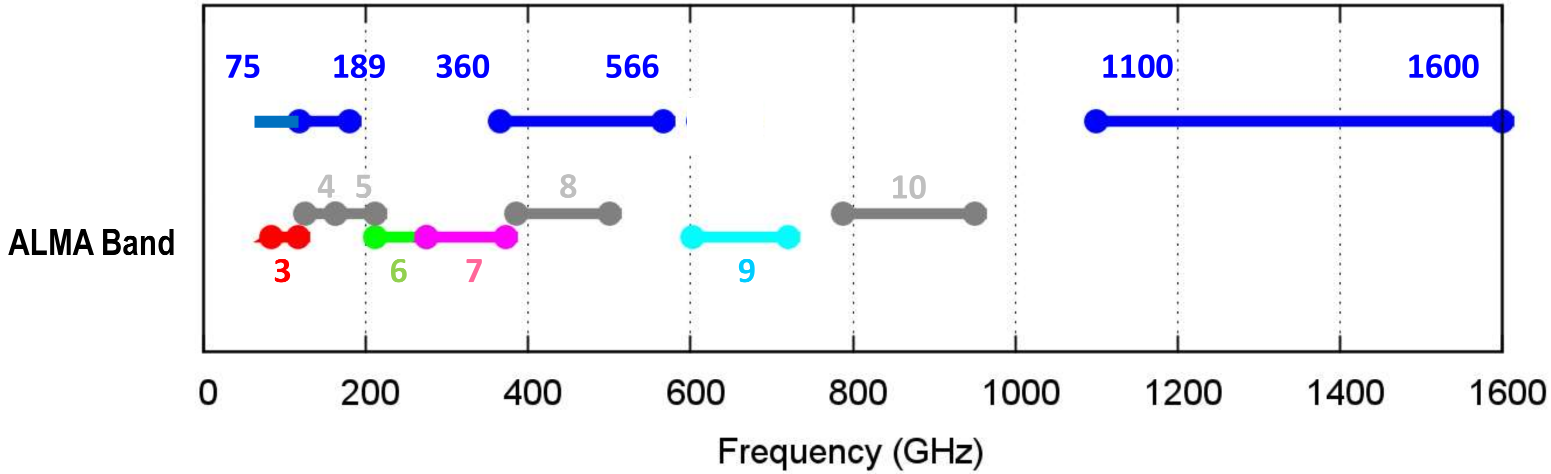
- Spectrometer sensitivity
- Production Efficiency
- Prediction Accuracy
- …

Spectrometer Sensitivity

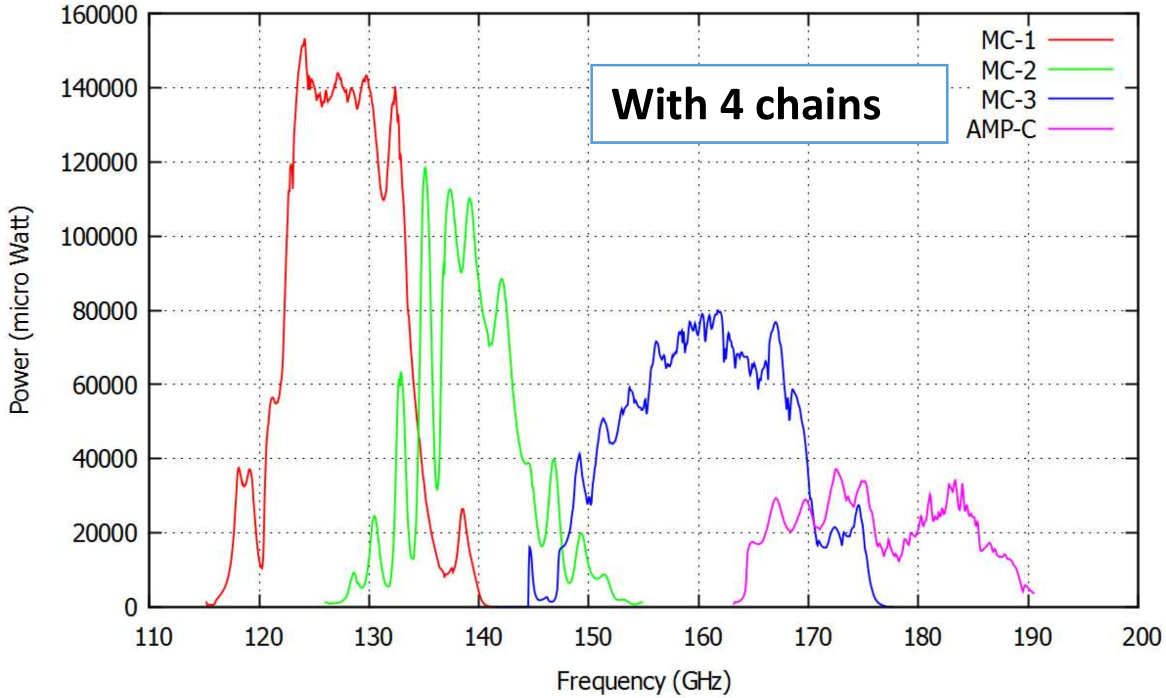
- Source noise vs Detector noise



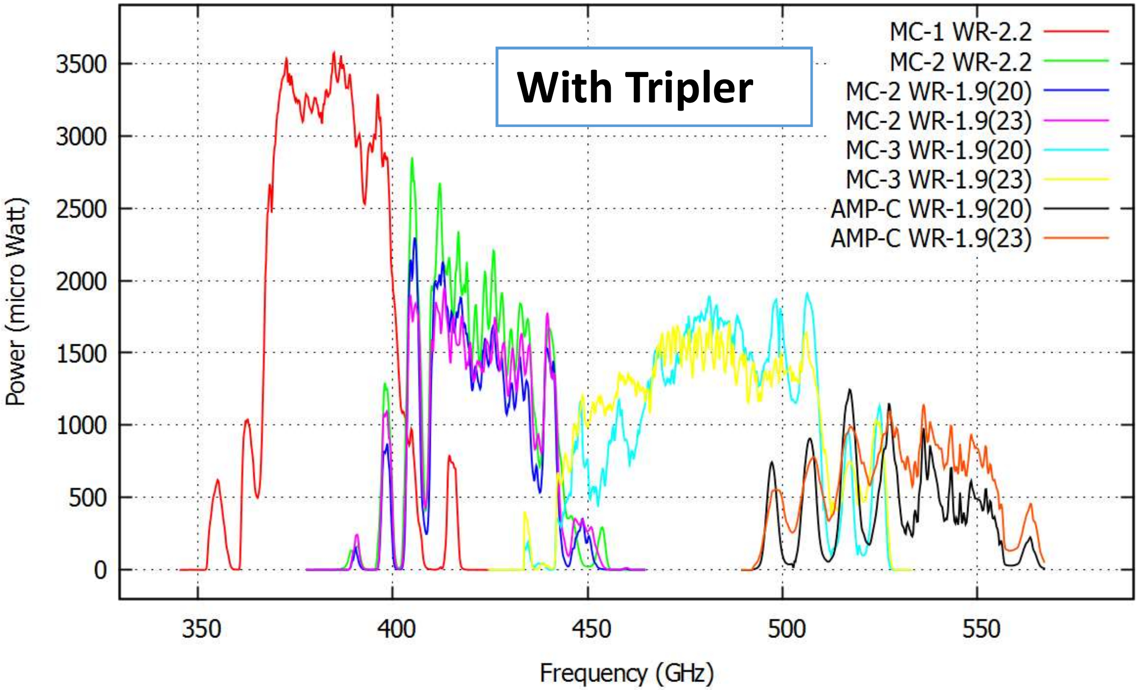
Frequency coverage



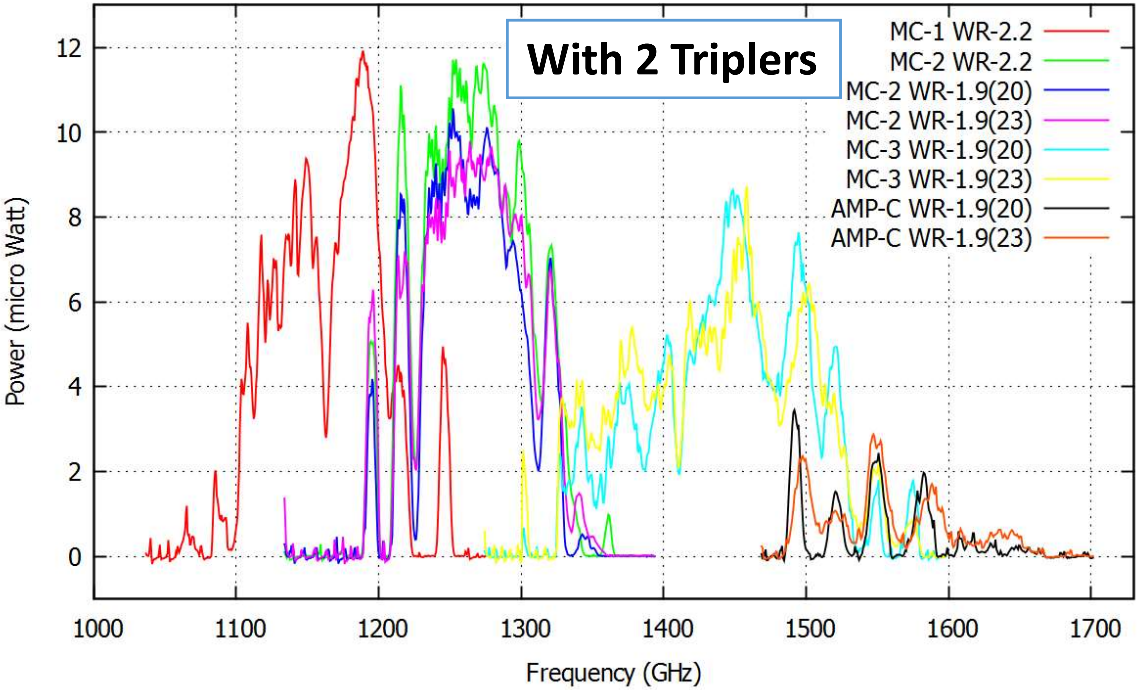
Frequency coverage



Frequency coverage



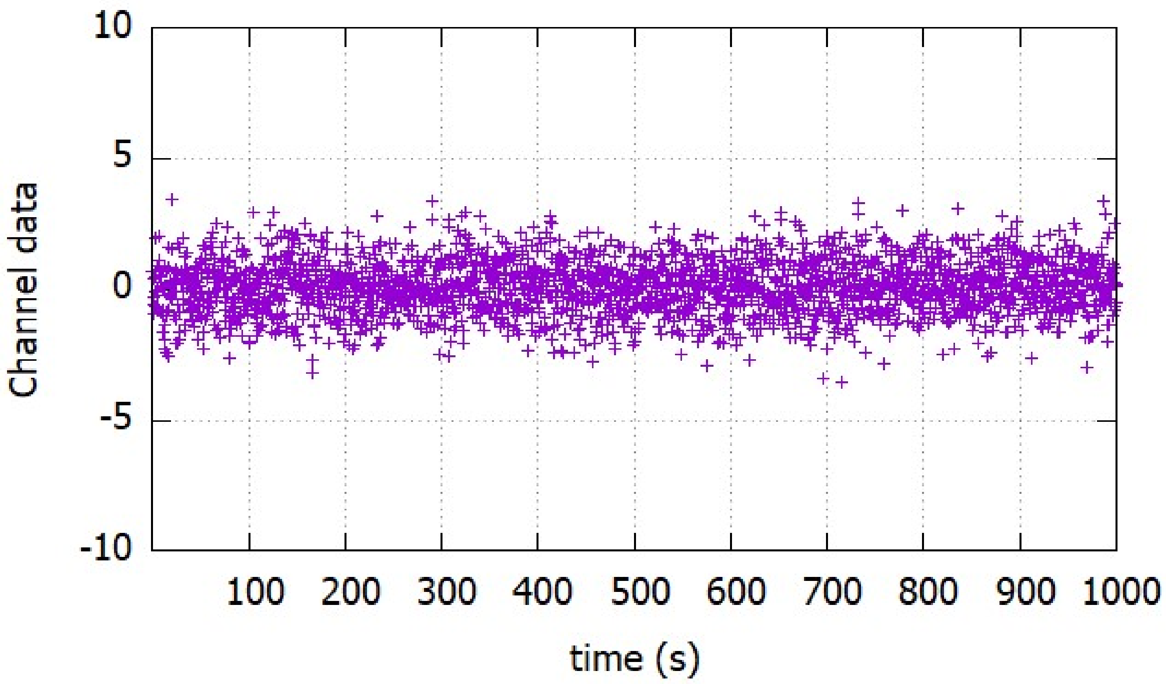
Frequency coverage



Other concerns

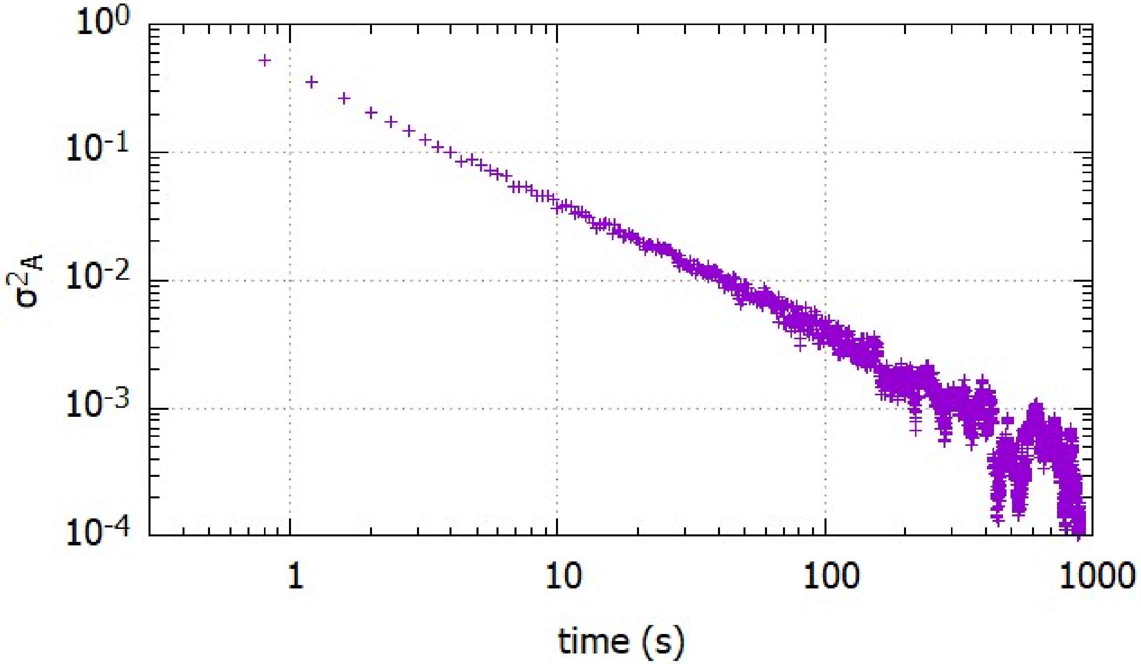
- Baseline distortion
- Discharge noise
- Earth magnetic field cancellation

Channel data vs Time (Accm. #)

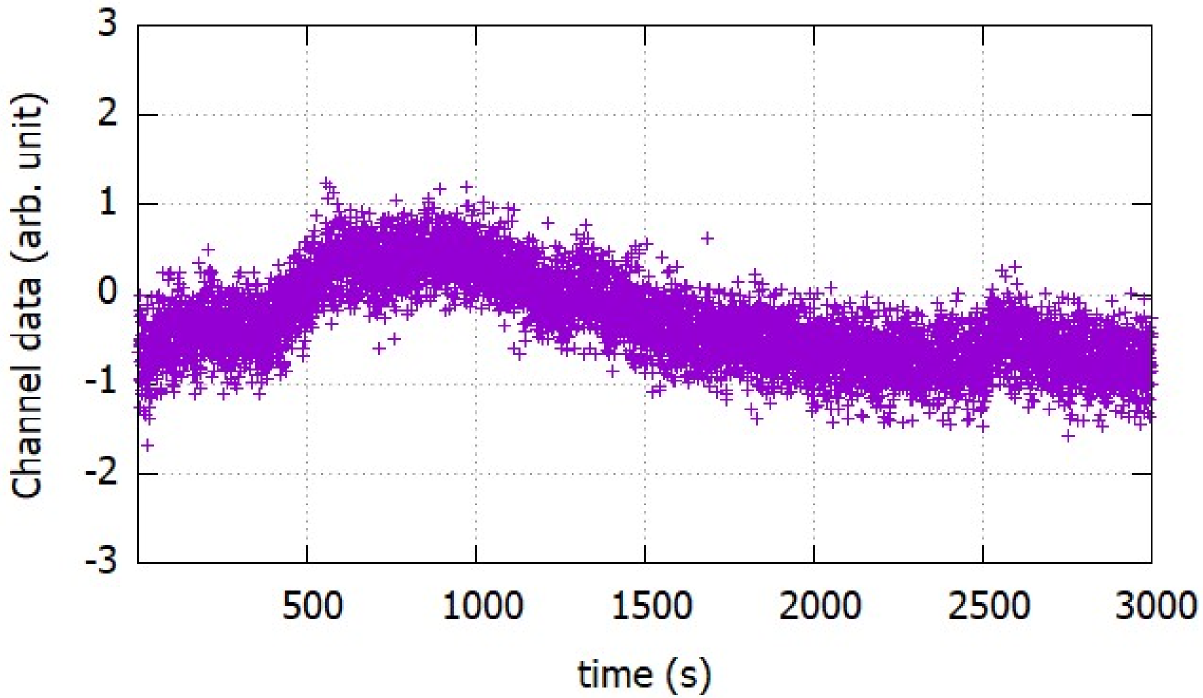


“Spectroscopic Allan Variance”

after R. Schieder



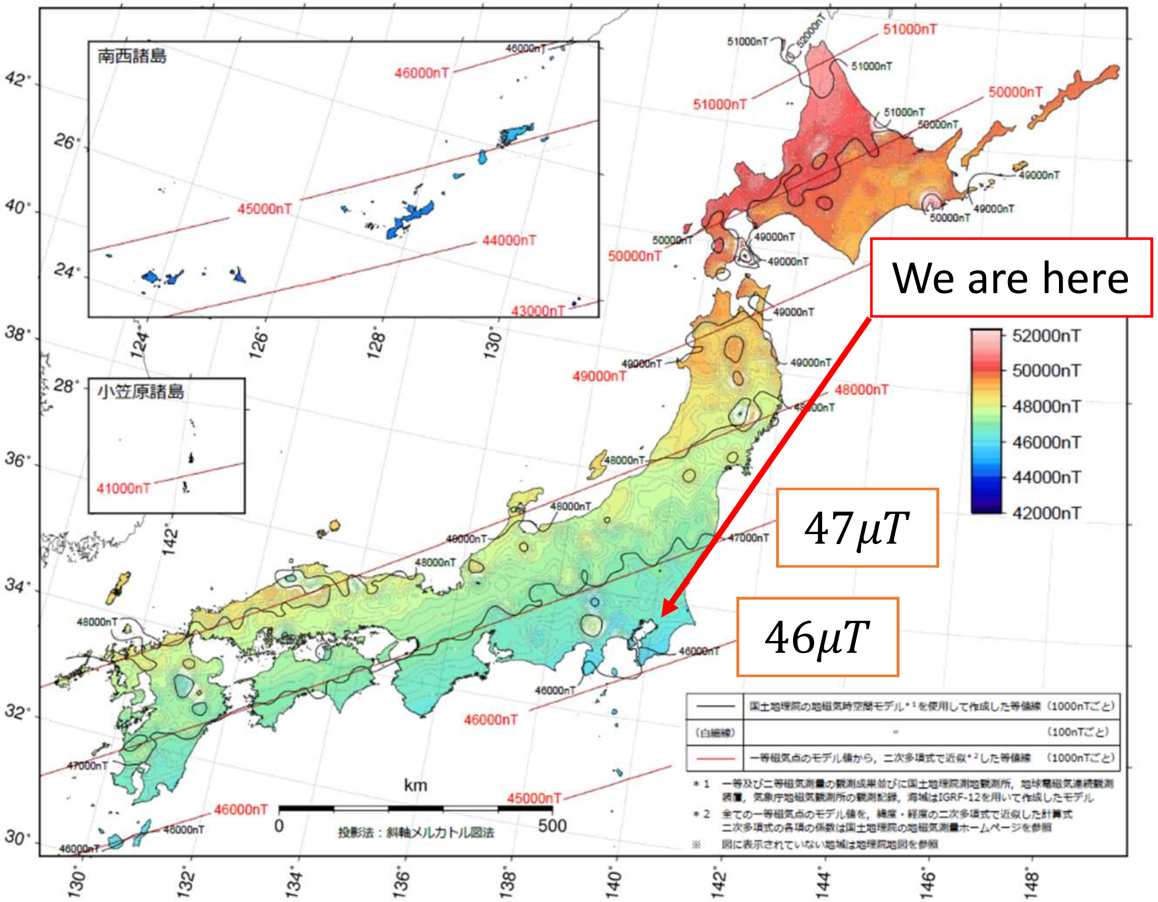
Channel data vs Time (Accm. #)



Other concerns

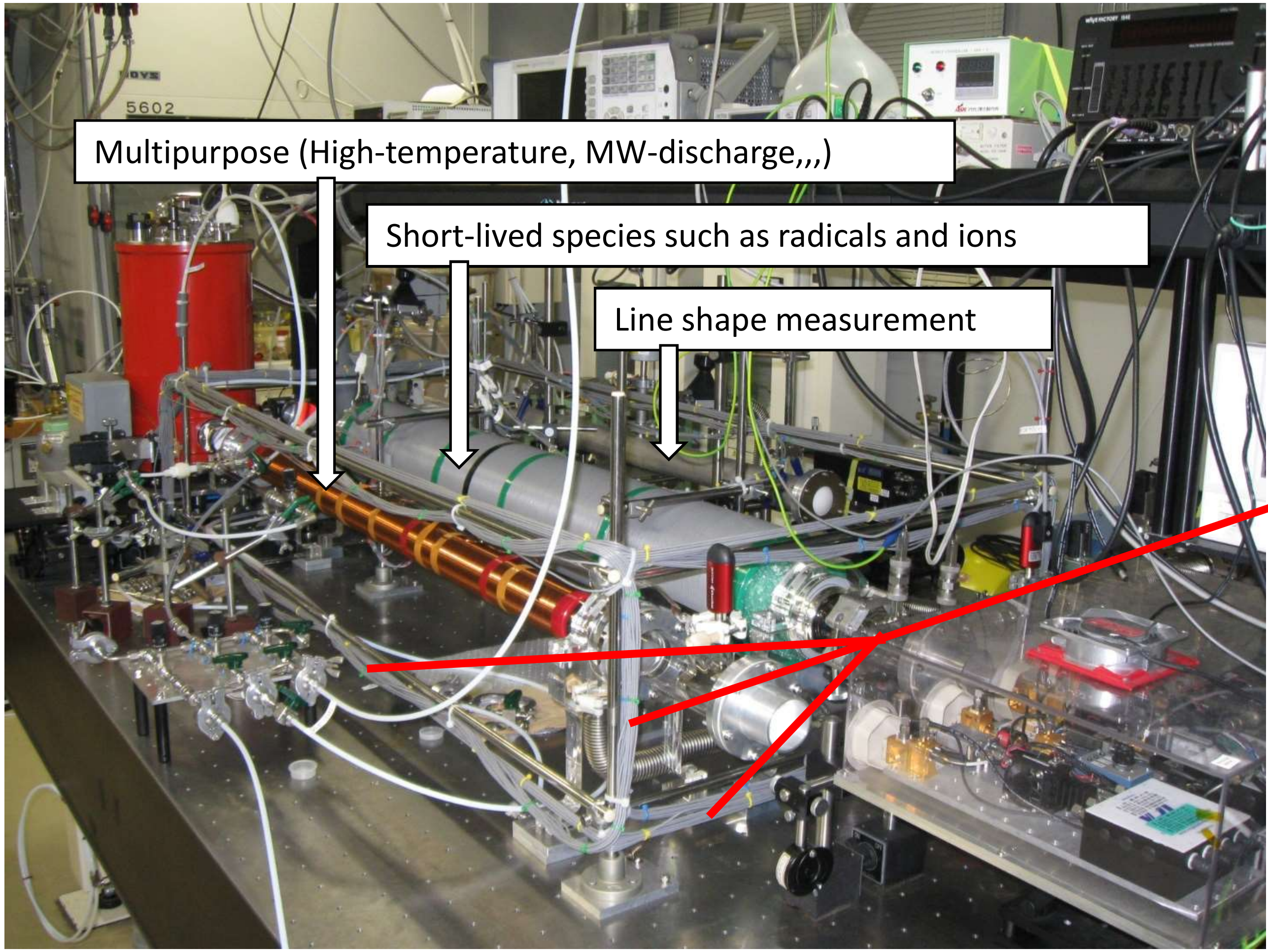
- Baseline distortion
- Discharge noise
- Earth magnetic field cancellation

Earth magnetic field



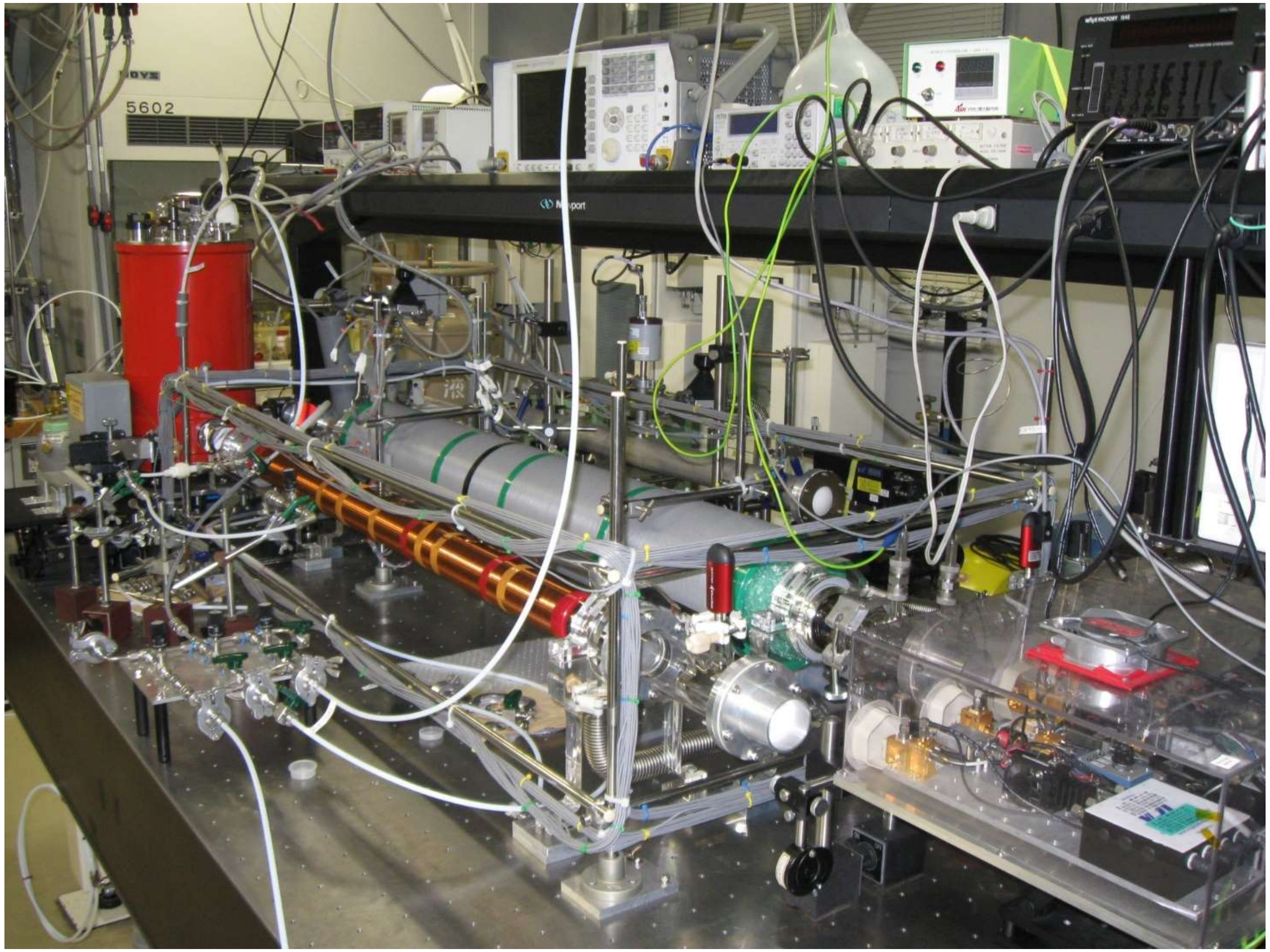
http://www.gsi.go.jp/common/000148086.pdf

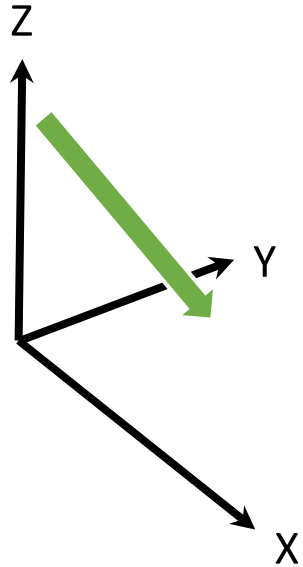
Spectrometer in Toho University (2018)



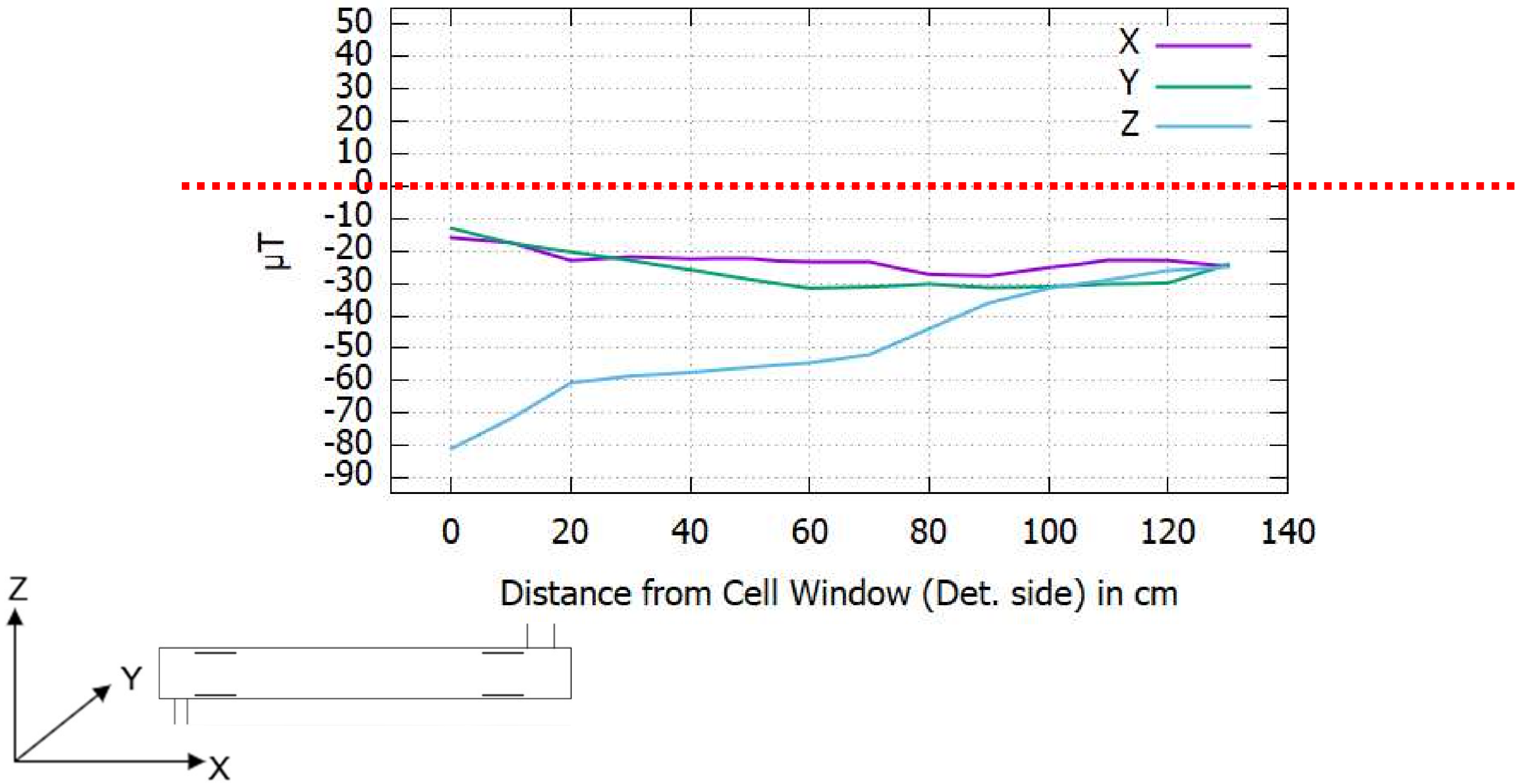
3 Pairs of Rectangular coils

Spectrometer in Toho University (2018)



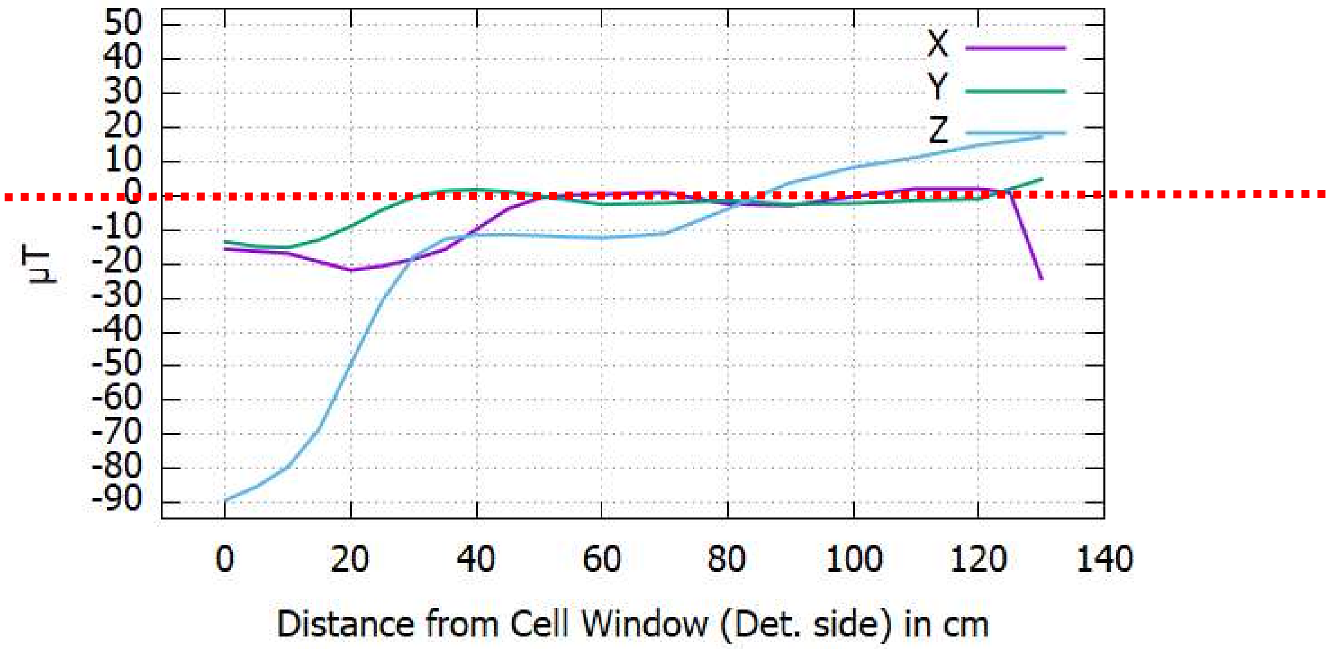


Magnetic field around spectrometer



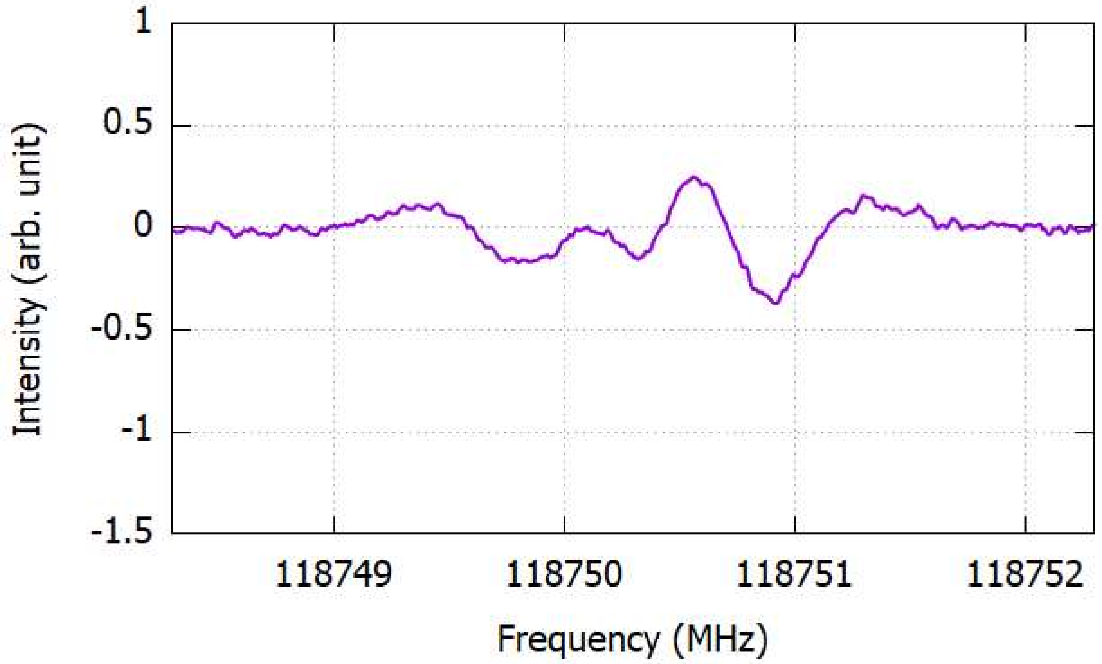
Magnetic field around spectrometer

After optimizing current setting of coils



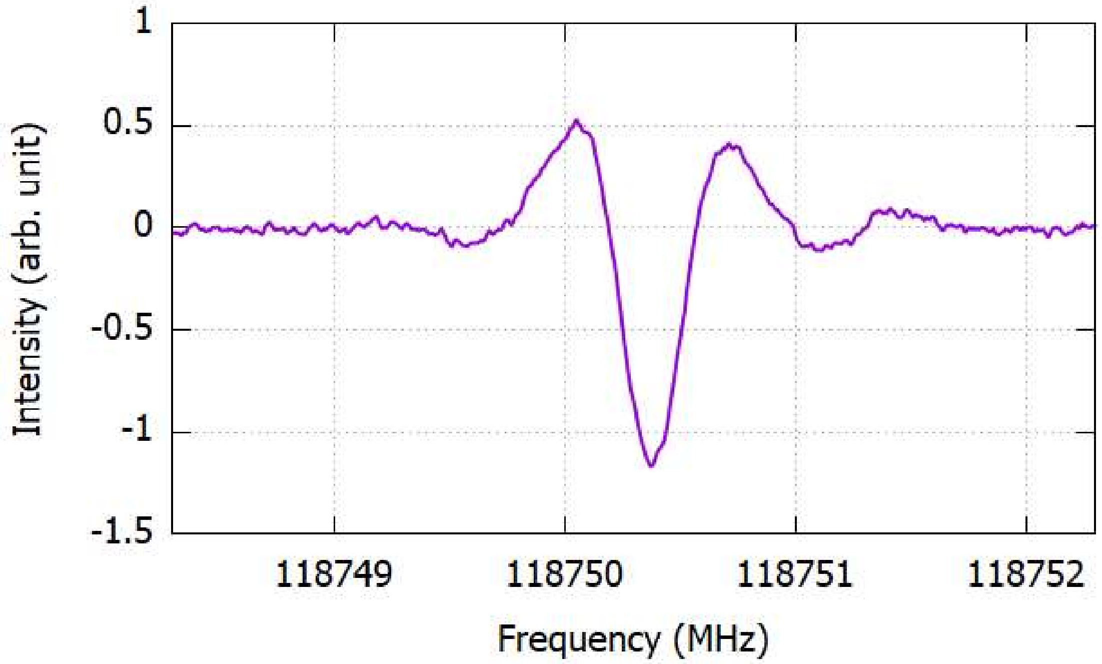
Oxygen line @118 GHz $(1_1\text{-}1_0)$

Before optimizing current setting of coils



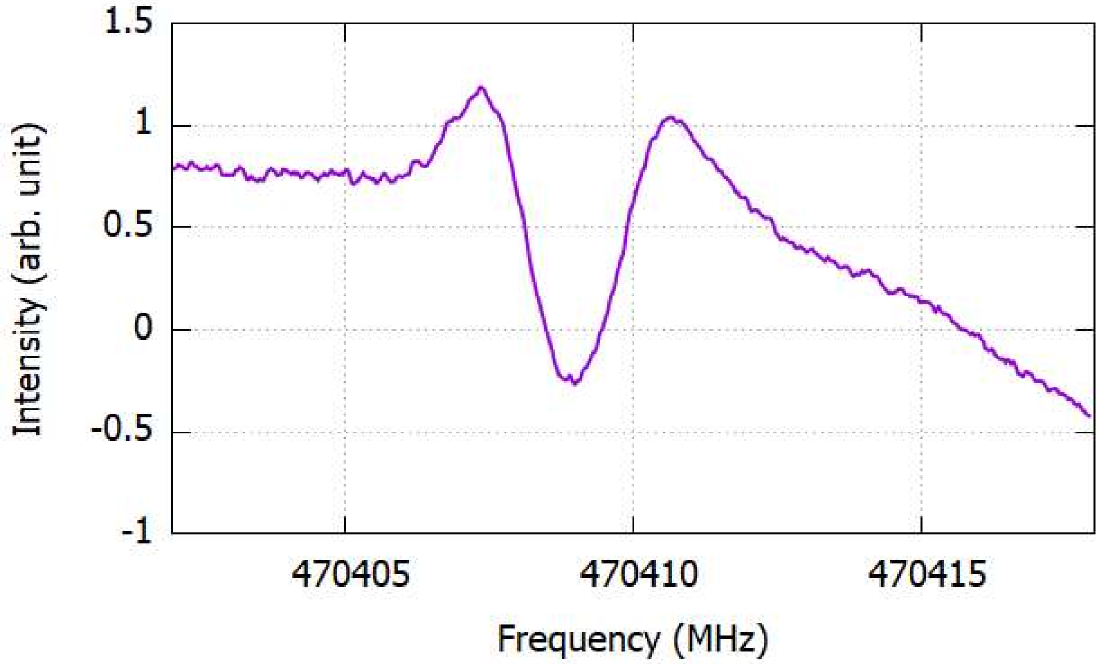
Oxygen line @118 GHz $(1_1\text{-}1_0)$

After optimizing current setting of coils



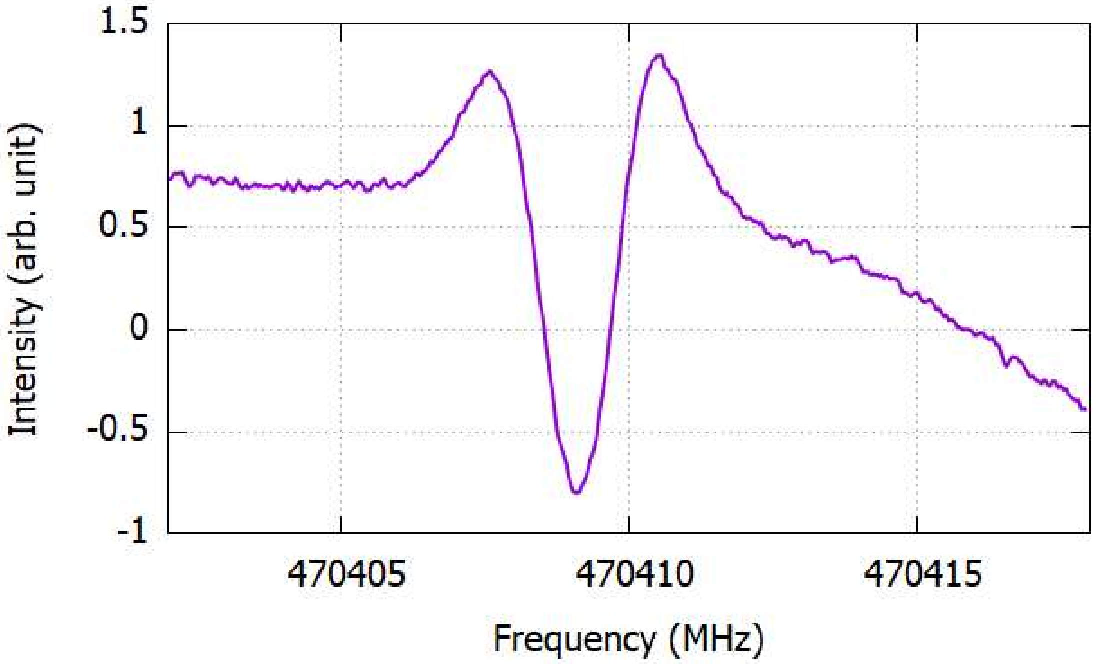
NH_2 radical @470 GHz (1_{10}-1_{01})

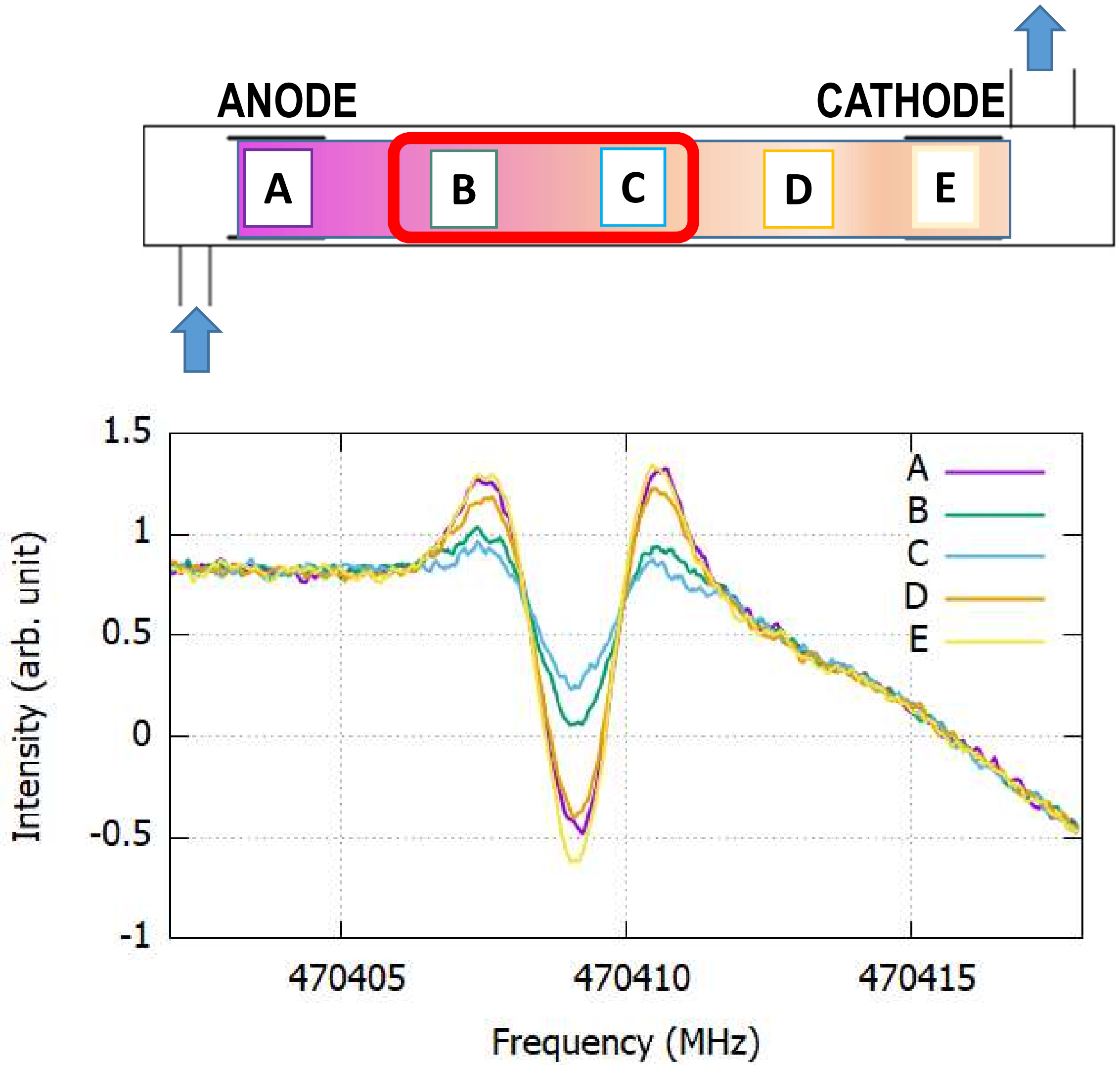
With current setting for observing oxygen line @ 118 GHz



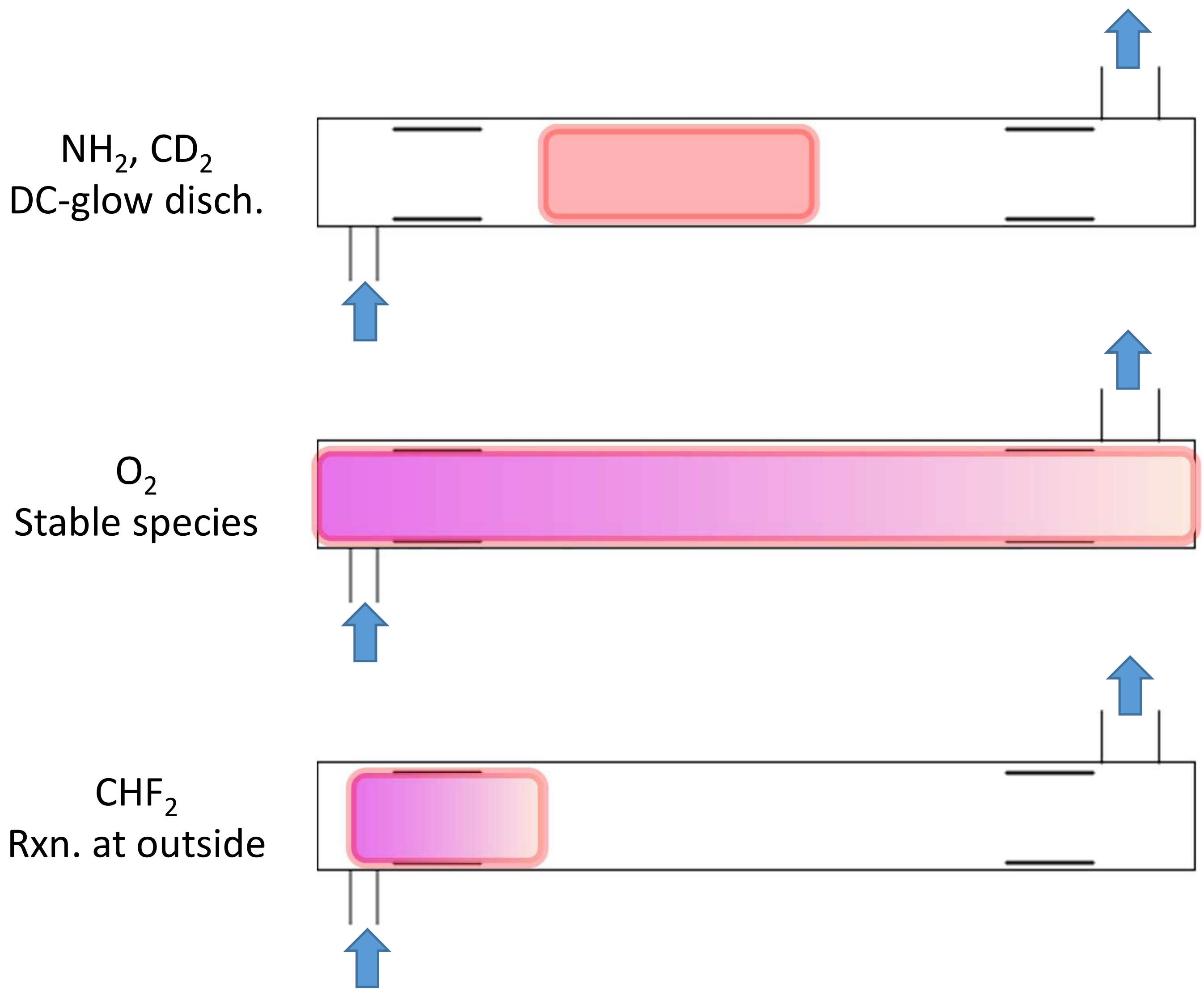
NH_2 radical @470 GHz (1_{10}-1_{01})

After re-optimization current setting of coils





NH_2 radical @470 GHz (1_{10}-1_{01})



NH_2, CD_2
DC-glow disch.
O_2
Stable species
CHF_2
Rxn. at outside

CD_2 : (Deuterated) Methylene radical

Difficult to produce enough amount for spectroscopy

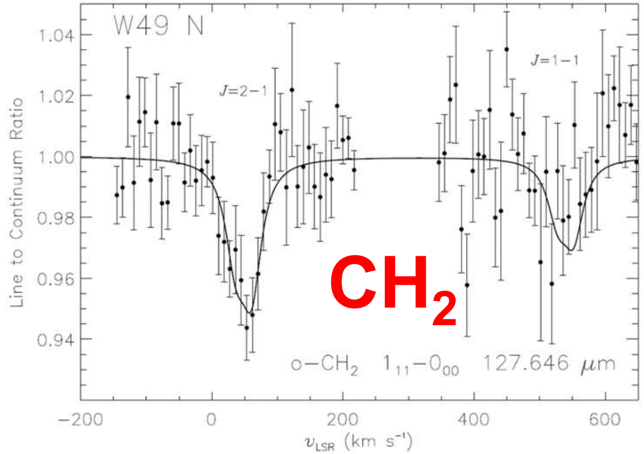
Methylene radical in space

- Relatively abundant in diffuse/dense interstellar cloud
- Most of astronomically important transitions lie in terahertz region

- Major production/Destruction Process

$CH_3^+ + e \rightarrow CH$ or CH_2

$CH_2 + O \rightarrow HCO$

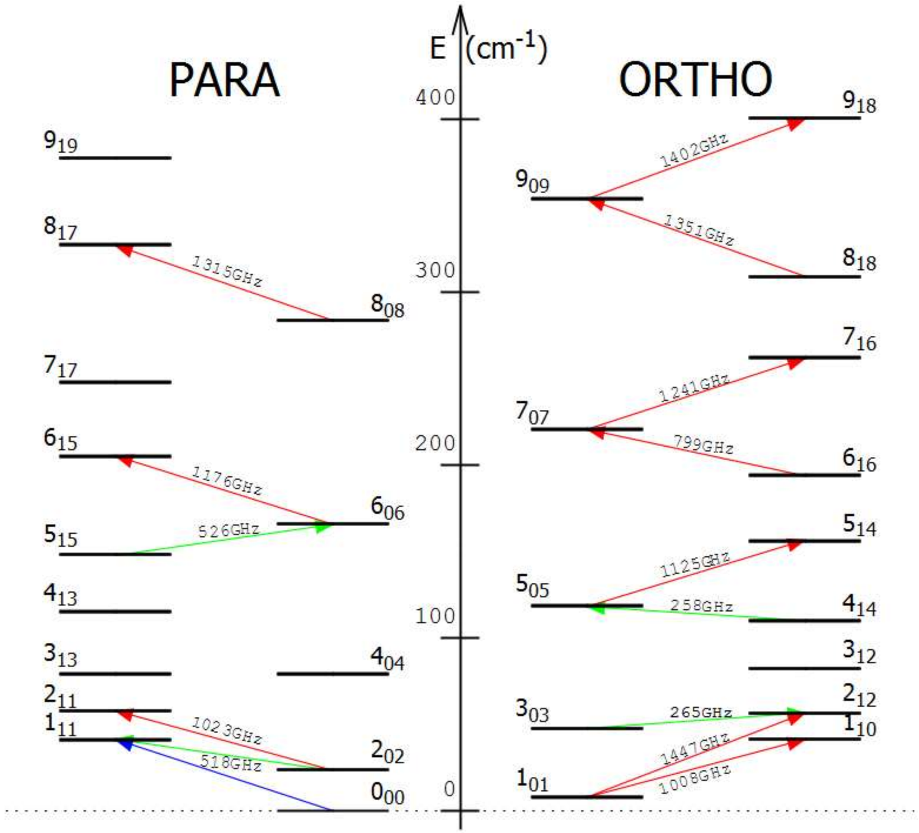


1_{11}-0_{00} transition (2350 GHz)
E. T. Polehampton et al. (2013)

Methylene radical in the ground state

CH_2	(THz Spectroscopy)	S. Brunken et al. (2004).
	(Global fit)	S. Brunken et al. (2005).
CHD	(LMR)	J. Nolte et al. (1994).
	(THz Spectroscopy)	H. Ozeki et al. (2011).
CD_2	(LMR)	K. M. Evenson et al. (1984).
	(MW Spectroscopy)	H. Ozeki et al (1996).
	(THz Spectroscopy)	**Present Work**

Energy level diagram of CD_2



# of	Transitions	Lines
Microwave	4	19
Terahertz	10	29

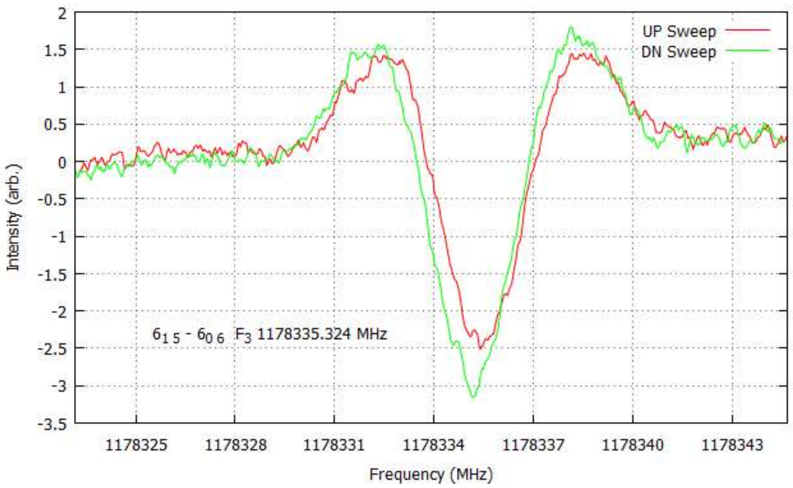
Terahertz

Microwave

Astronomically Important Transitions

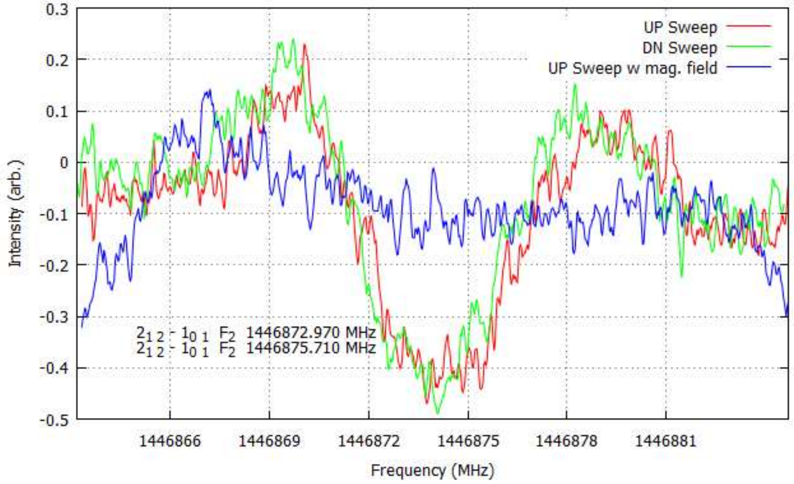
CD_2 : Transitions with K_a = 1 - 0

Para-CD_2 @ 1178 GHz



6_{15}-6_{06} F_3

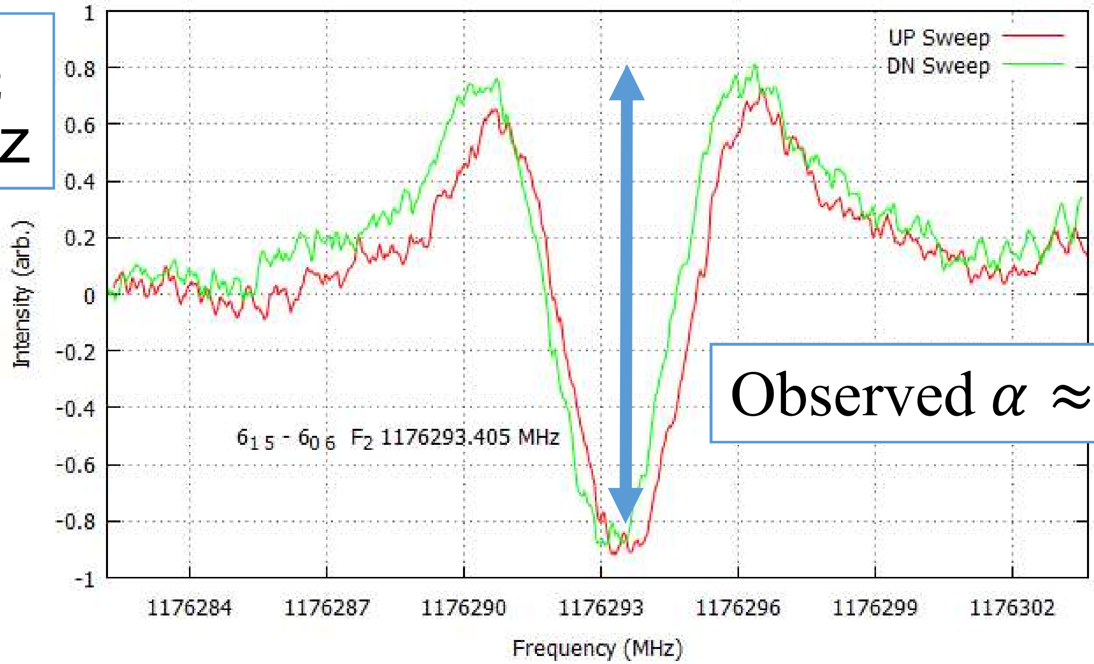
Ortho-CD_2 @ 1446 GHz



2_{12}-1_{01} F_2

Estimation of production efficiency

$6_{15} - 6_{06}\ F_2$
@1176 GHz



Observed $\alpha \approx 10^{-5}\ cm^{-1}$

Estimation of production efficiency

- Experimental condition
  - Total Pressure 5 Pa
  - Cell length 150 cm

- Observed optical thickness
  ➔ $\sim 1.5 \times 10^{-3}$

- Calculated spectral Intensity

Log (I) @ 300 K (nm^2MHz)	*F'' – F'*
-2.409	7-7
-2.547	5-5
-2.483	6-6
-2.00	(total)

- Expected optical thickness @ 100 % production efficiency
  ➔ ~ 6.7

$\eta \sim 0.02$ %

Demand for more efficient production

- $CD_4 \text{ in Ar} \xrightarrow{\text{DC-glow disch.}} CD_2$
- $CD_4 + F \longrightarrow CD_2$
- $CD_4 \xrightarrow{Ar^* \text{or } He^*} CD_2$

- $(CD_2CO)_2 \xrightarrow{\Delta\ (800K)} CD_2CO \xrightarrow{\text{DC-glow disch.}} CD_2$
- $(CD_3CO)_2O \xrightarrow{\Delta\ (800K)} CD_2CO + CD_3COOD \xrightarrow{\text{DC-glow disch.}} CD_2$
- ???

Molecular constants of CD_2

Constants	Present Work	FIR-LMR[a]
A	1132826.442(110)[b]	1132820.6(18)
B	126805.268(34)	126804.1(34)
C	110760.770(24)	110760.1(34)
Δ_J	2.80044(124)	2.771(19)
Δ_{JK}	-141.1343(101)	-149.16(24)
Δ_K	16795.21[c]	16795.21(48)
δ_J	0.65606(32)	0.669(7)
δ_K	83.4[c]	83.4(15)
Φ_J	-0.0002631(43)	
Φ_{JK}	-0.07739(47)	-0.057(5)
Φ_K	588.[c]	588.[c]

Molecular constants of CD_2 (Cont'd)

Constants	Present Work	FIR-LMR[a]
ε_{aa}	10.674(240)	8.5(11)
ε_{bb}	-76.190(48)	-78.3(11)
ε_{cc}	-62.425(65)	-62.4(119
α	7770.115(147)	7759.3(9)
α_K	-40.827(168)	
β	1222.897(149)	1216.6(9)
$a_F(D)$	-2.903(141)	
$T_{aa}(D)$	5.036(57)	
$T_{bb}(D)-T_{cc}(D)$	-0.076	

[a] K. M. Evenson et al (1984).

[b] 1σ

[c] fixed

NHD : (Mono-Deuterated) Amidogen radical

Relatively easy to produce, but hard to analyze the spectra

Mono-deuterated Amidogen NHD

- Amidogen : Relatively easy to produce

  : Light molecule

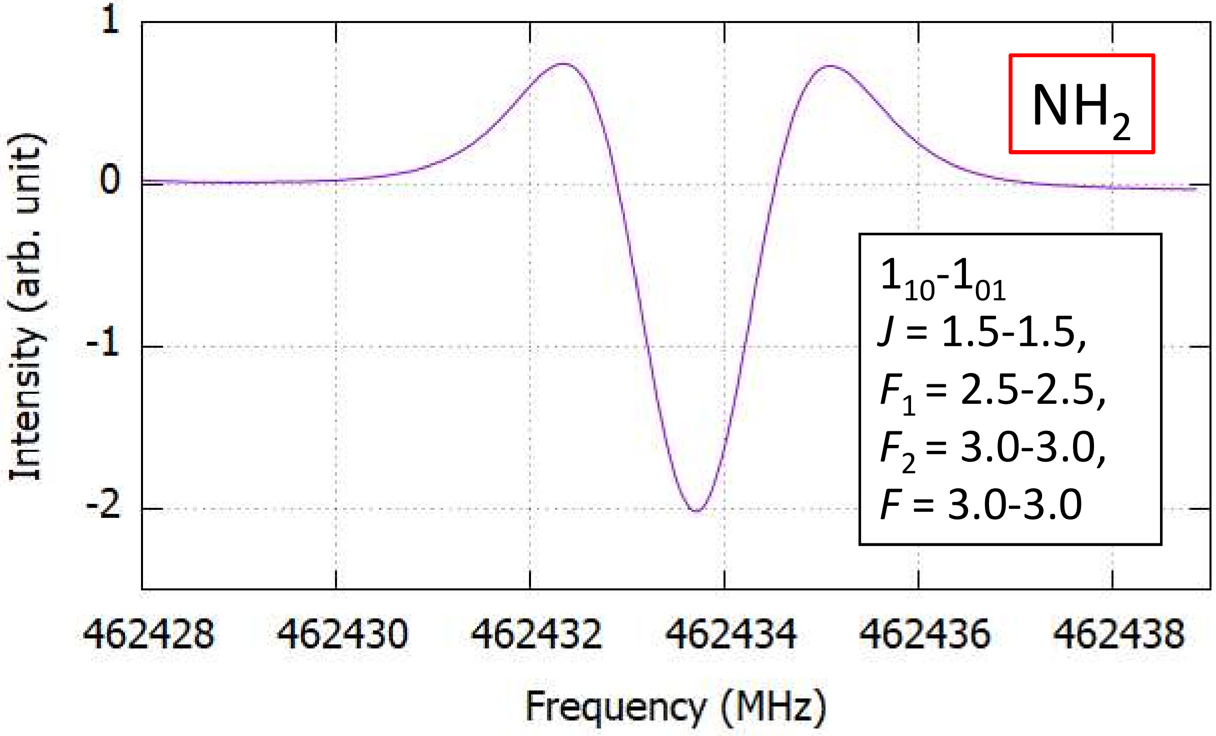
  ➔ Major transitions lie in the terahertz region

NHD : 4 spin system : S + I(N) + I(H) + I(D)

➔ Gives complex fine & hyperfine spectra

Amidogen : easier to produce than Methylene

DC-glow dish. of NH_3 in Ar



Production efficiency $\eta > 1\%$

Complex fine & hyperfine spectra

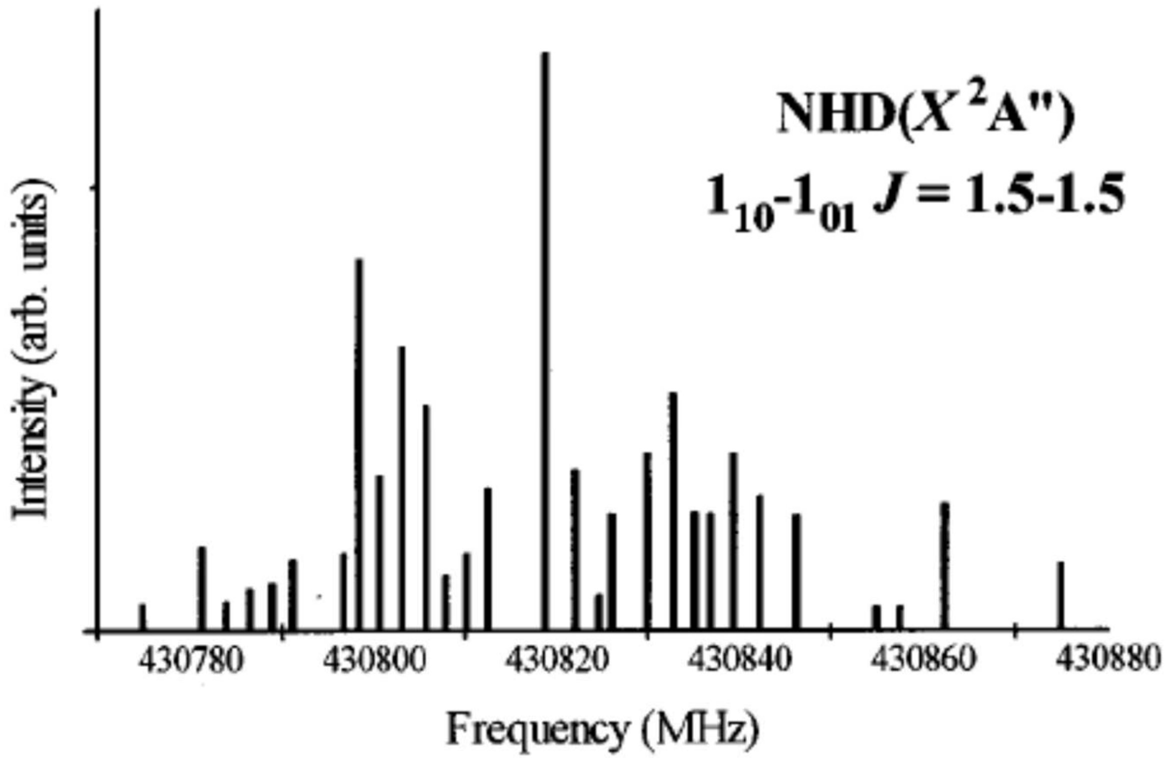
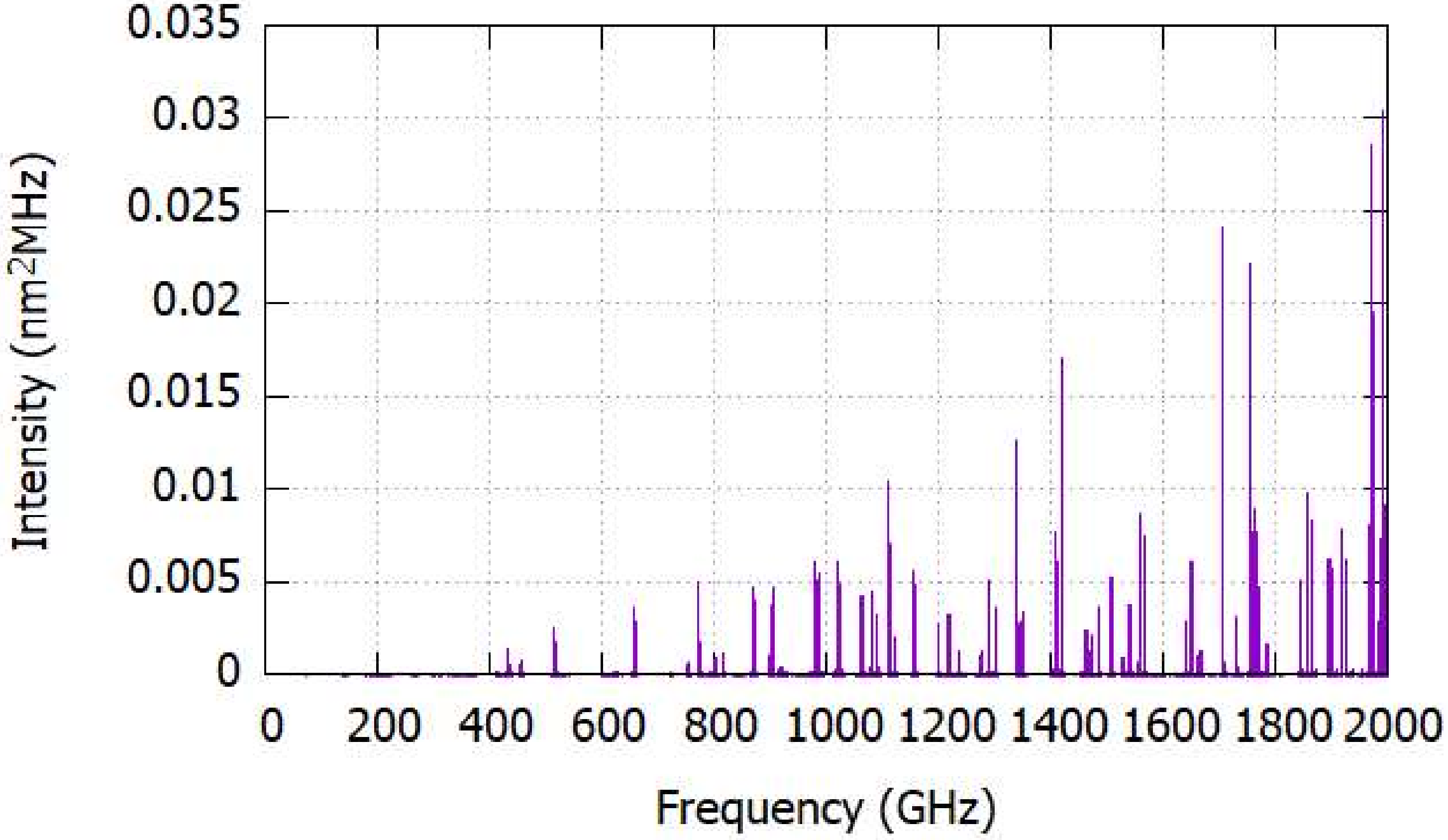


FIG. 2. The stick diagram of $1_{10}-1_{01}$ $J=1.5-1.5$ transition of NHD ($X\,^2A''$) in the 430 GHz region with observed relative intensities.

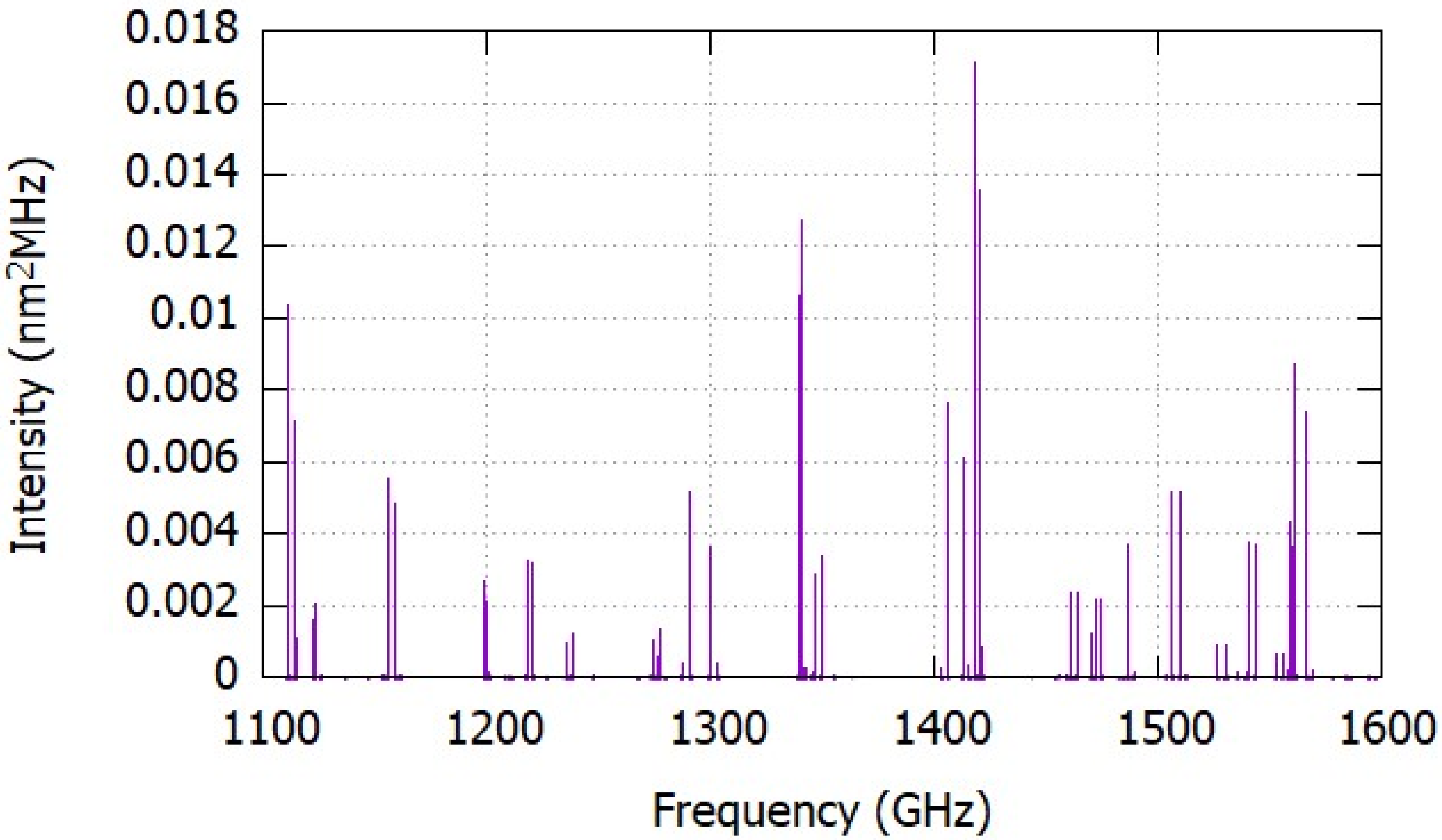
K. Kobayashi et al. (1997)

NHD @ 300 K



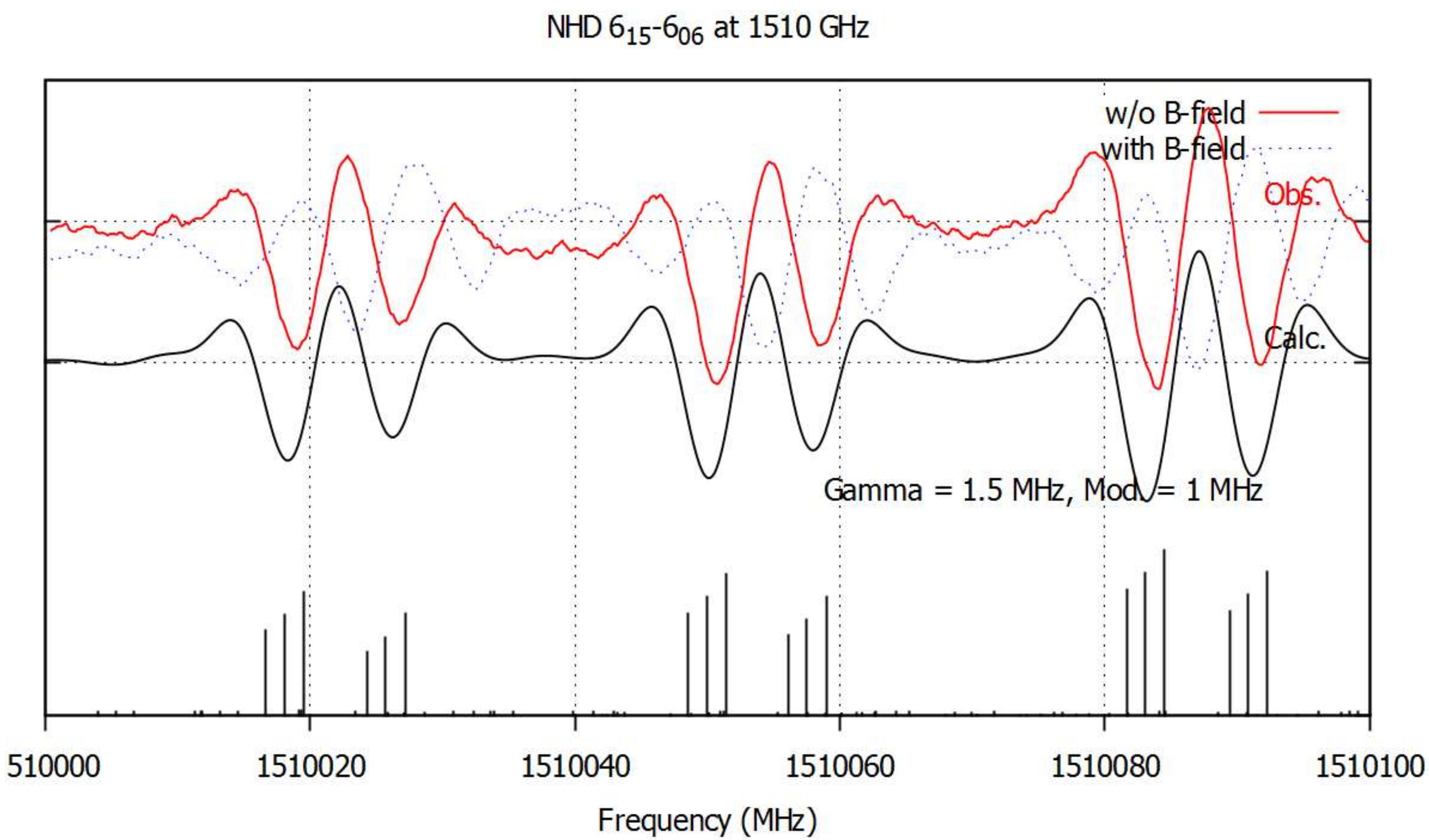
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
Intensity (nm²MHz)
0
200
400
600
800
1000
1200
1400
1600
1800
2000
Frequency (GHz)

NHD @ 300 K

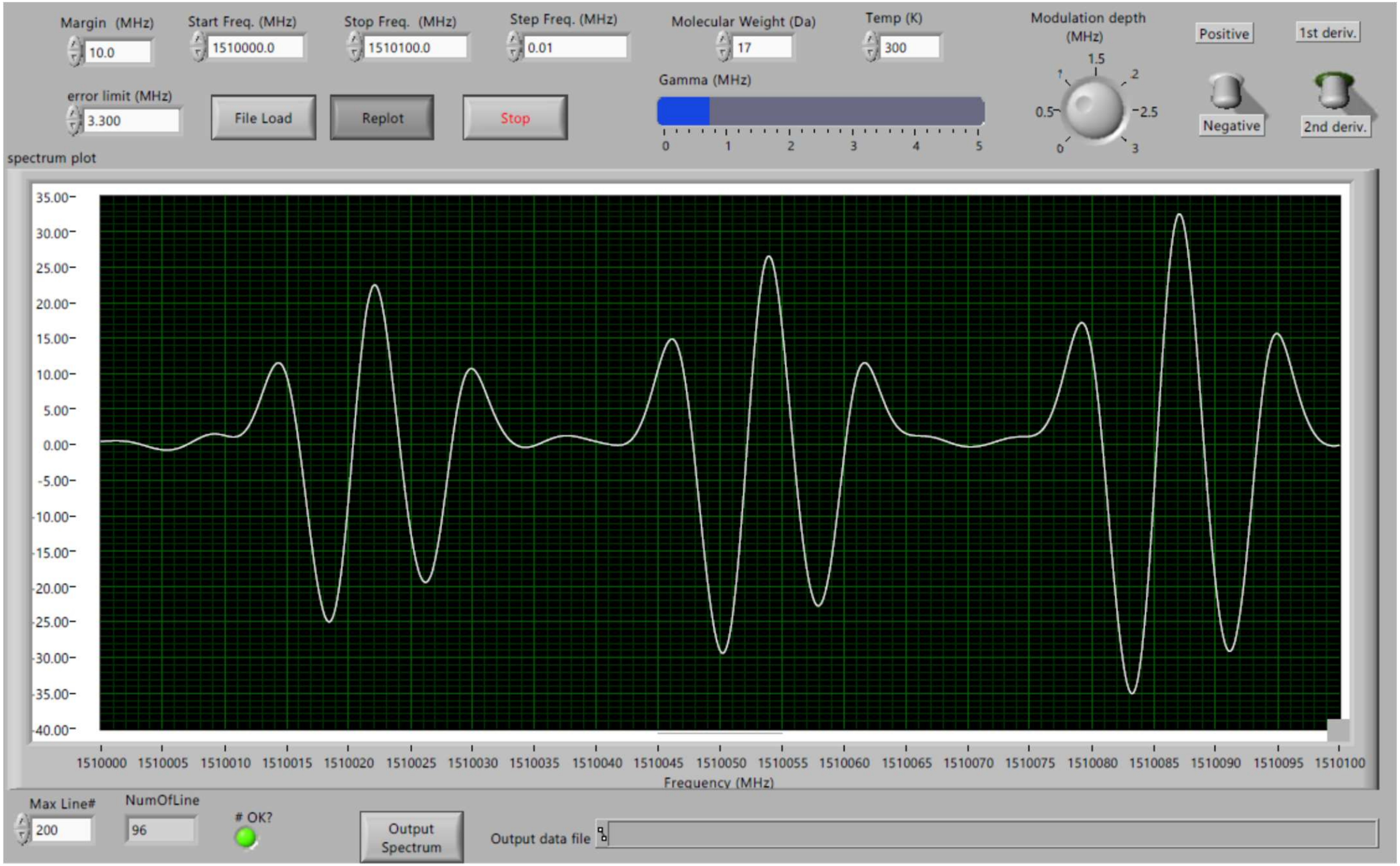


Intensity (nm2MHz)
0.018
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
1100
1200
1300
1400
1500
1600
Frequency (GHz)

Case 1 (OK)

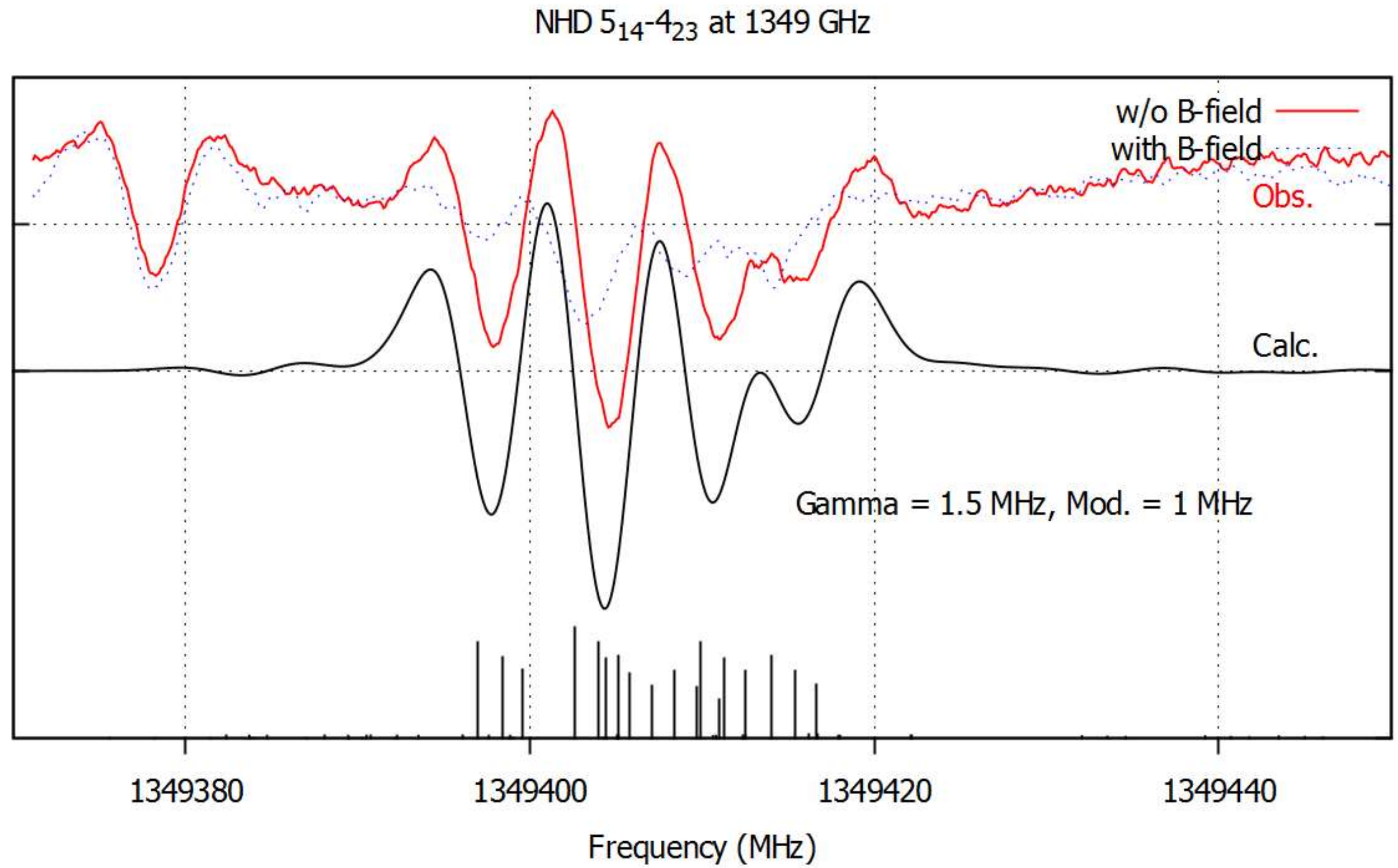


NHD 6_{15}-6_{06} at 1510 GHz
w/o B-field
with B-field
Obs.
Calc.
Gamma = 1.5 MHz, Mod. = 1 MHz
510000
1510020
1510040
1510060
1510080
1510100
Frequency (MHz)



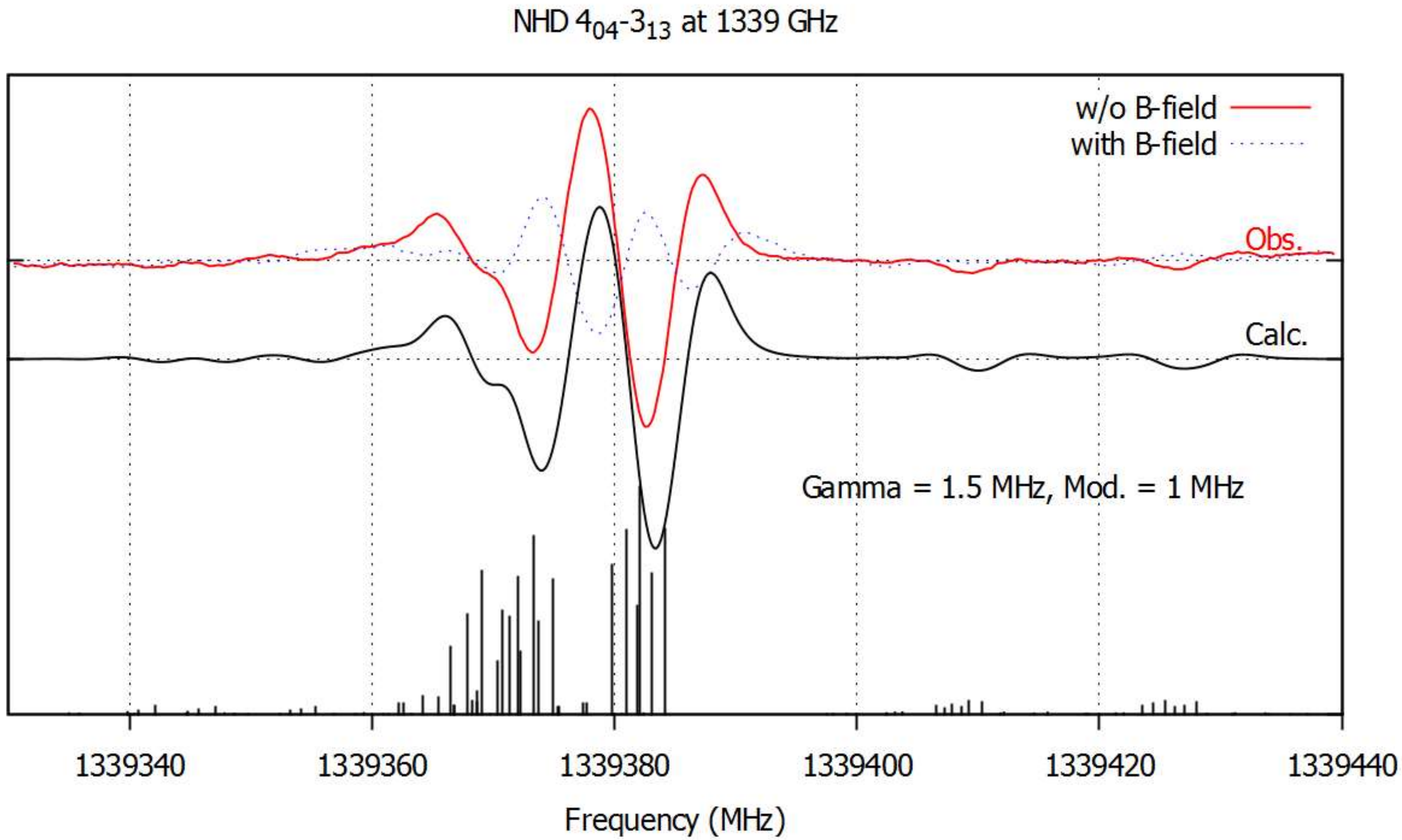
Margin (MHz)
10.0
Start Freq. (MHz)
1510000.0
Stop Freq. (MHz)
1510100.0
Step Freq. (MHz)
0.01
Molecular Weight (Da)
17
Temp (K)
300
Modulation depth (MHz)
Positive
1st deriv.
error limit (MHz)
3.300
File Load
Replot
Stop
Gamma (MHz)
Negative
2nd deriv.
spectrum plot
Frequency (MHz)
Max Line#
200
NumOfLine
96
OK?
Output Spectrum
Output data file

Case 2 (NG)

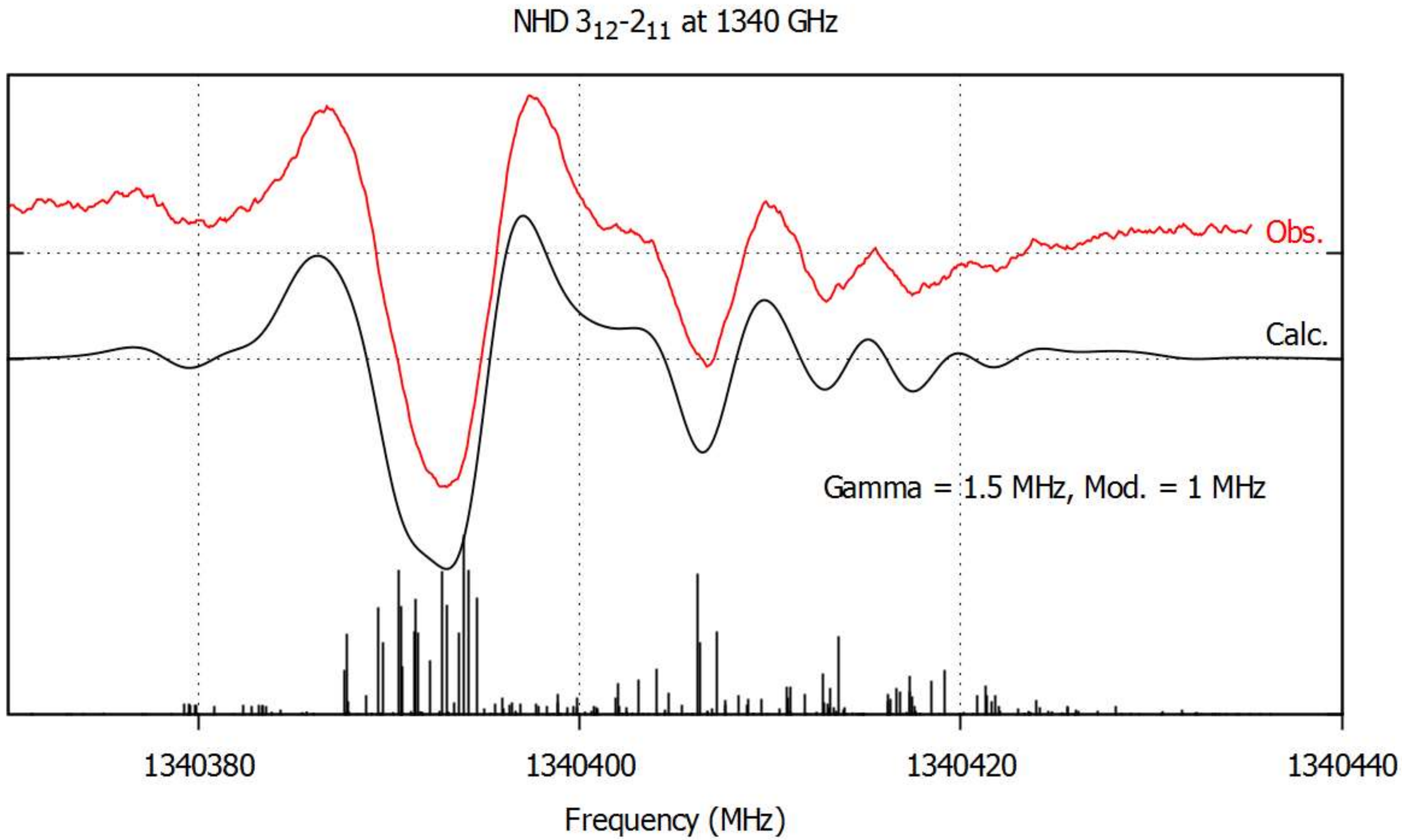


NHD 5_{14}-4_{23} at 1349 GHz
w/o B-field
with B-field
Obs.
Calc.
Gamma = 1.5 MHz, Mod. = 1 MHz
1349380
1349400
1349420
1349440
Frequency (MHz)

Case 3 (NG)


NHD 4_{04}-3_{13} at 1339 GHz
w/o B-field
with B-field
Obs.
Calc.
Gamma = 1.5 MHz, Mod. = 1 MHz
1339340
1339360
1339380
1339400
1339420
1339440
Frequency (MHz)

Case 4 (NG)


NHD 3_{12}-2_{11} at 1340 GHz
Obs.
Calc.
Gamma = 1.5 MHz, Mod. = 1 MHz
1340380
1340400
1340420
1340440
Frequency (MHz)

Analysis of spectral profile obtained by frequency modulation technique

- Calculated spectral line profile $S(\nu - \nu_o)$ is obtained by Fourier transformation of molecular polarization correlation function $\Phi(t)$, as
- $$S(\nu - \nu_0) = I_o \cdot \exp\left[-\Re\left(\mathcal{F}\left(J_2\left[mt \cdot \mathrm{sinc}\left(\frac{\omega_m t}{2}\right)\right]\cos(\omega_m t) \cdot \Phi(t)\right)\right) \cdot L\right]$$
$$+\ baseline\ correction$$

- $\Phi(t)$ for each profile model is:

Voigt : $\Phi_V(t) = \exp\left[i\omega_0 t - \Gamma_0 t - \left(\frac{kv_{a0}t}{2}\right)^2\right]$

Galatry : $\Phi_G(t) = \exp\left[i\omega_0 t - \Gamma_0 t + \frac{1}{2}\left(\frac{kv_{a0}t}{\beta}\right)^2 \cdot \{1 - \beta t - \exp(-\beta t)\}\right]$

Speed Dependent Voigt : $\Phi_{SDV}(t) = \frac{\exp\left[i\omega_0 t - \left(\Gamma_0 - \frac{3}{2}\Gamma_2\right)t\right]}{(1+\Gamma_2 t)^{3/2}} \cdot \exp\left[-\frac{(kv_{a0}t)^2}{4(1+\Gamma_2 t)}\right]$

NHD so far,,,

- 16 Rotational transitions are measured in the THz region (1.1 -1.6 THz)
- Some observed frequencies cannot be included in the fit due to complicated hyperfine structure
- Dedicated program for hyperfine structure envelope analysis must be developed

CHF_2 : Di-fluoro methyl radical

Produce radical by MW disch. : Analysis of Tunneling motion

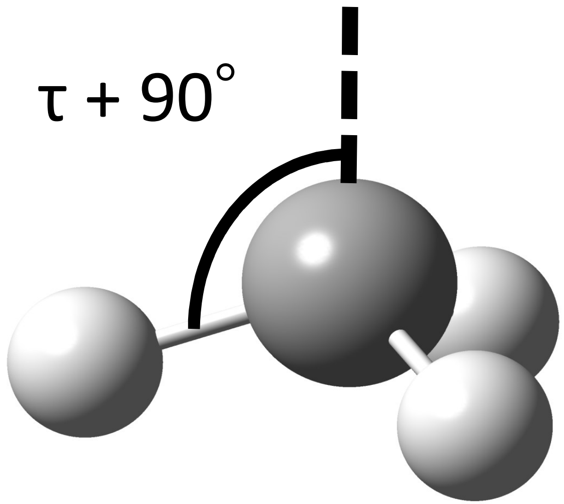
Molecular structures of fluoromethyl radicals CH_xF_{3-x} (x = 0 - 3)

- **Vary from planar (x = 0) to umbrella (x = 3)**

τ	CH_3	CH_2F	CHF_2	CF_3
MW / IR	0° [1]	≒0° [2]	**This Work**	18.15° [3]
ESR[4]	0°	< 5°	12.7°	17.8°

[1] **C. Yamada et al., (1981)**
[2] **Y. Endo et al., (1983)**
[3] **Y. Endo et al., (1982)**
[4] **Fessenden & Shuler (1965)**

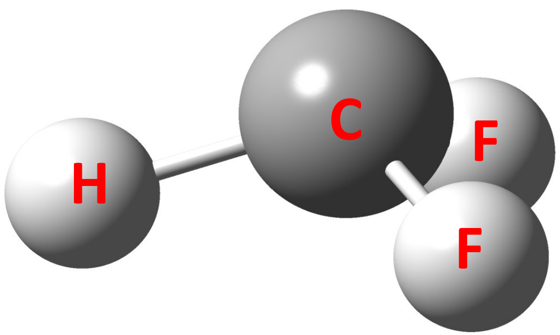
> "We may then expect that either or both of the two "intermediate" species CH_2F and **CHF_2 show** the effect of **inversion doubling** in its high-resolution spectra"
>
> E. Hirota ,in "*High-resolution Spectroscopy of Transient Molecules* "



Definition of out-of-plane angle τ

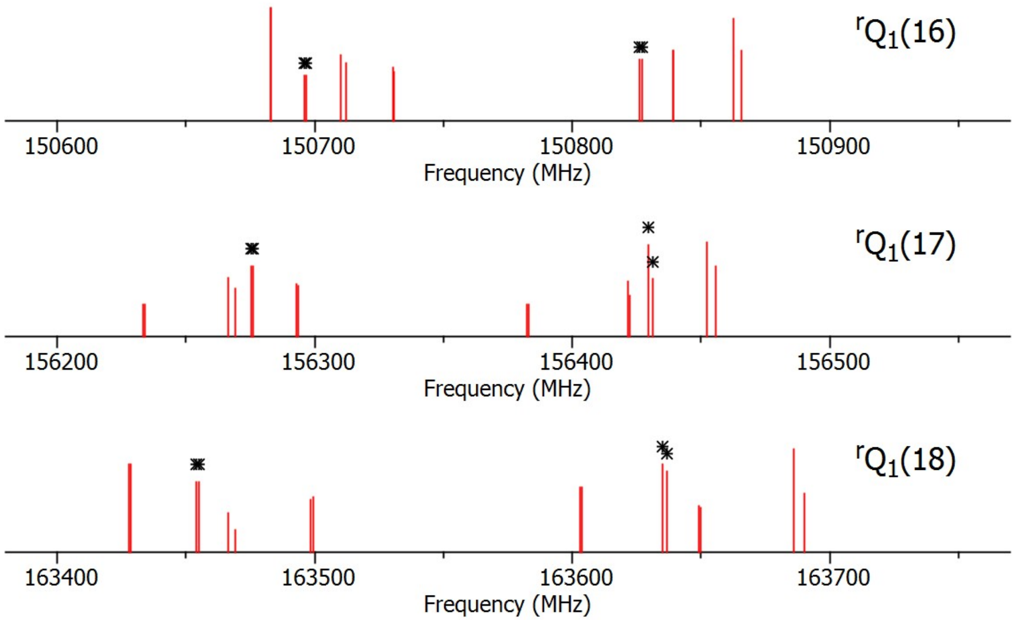
Spectral Observation

- Radical produced by
  F(MW-disch. of CF_4) + CH_2F_2
- Spectrum observed in 90 – 400 GHz region and assigned 32 *b*-type rotational transitions (below 200 GHz)



Observed spectra & Initial Analysis

- 4 spin system : $S+I(F_{tot})+I(H)$, $I(F_{tot})=I(F_1)+I(F_2)$
- Composite hyperfine structure of one H and two F nuclei giving $I_F = 0$ (singlet or para) and $I_F = 1$ (triplet or ortho)

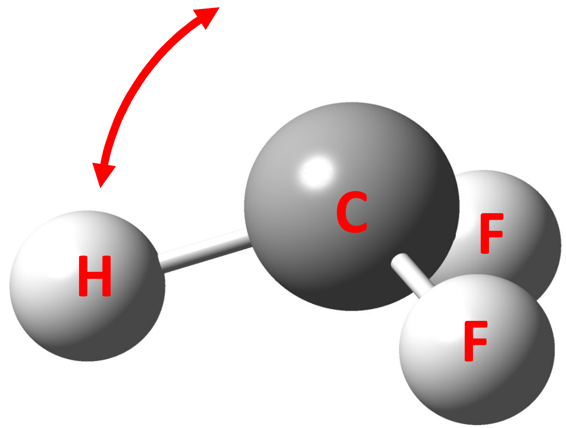


Stick diagram of observed hyperfine structure for the $^rQ_1$ branch transitions with N = 16 - 18.
Asterisks indicate the hyperfine components of $I_F = 0$

Hyperfine structure of CHF_2

- 4 spin system : $S+I(F_{tot})+I(H)$, $I(F_{tot})=I(F_1)+I(F_2)$
- Composite hyperfine structure of one H and two F nuclei giving

  I_F = 0 (singlet or para) and I_F = 1 (triplet or ortho)
- Line frequencies of singlet changed **zigzag** relative to those of triplet



<u>Hyperfine structure alternation in the inversion levels</u>

Inada et al. CPL (1998)

Conclusions

- Spectroscopy of short-lived species are interesting due to its diversity in many aspects such as production, analysis,,

From e-mail exchange more than 10 years ago,,,

> Sounds like a lot of fun with lots of spins > 0 !
>
> *by Holger S. P. Müller*

> I fully agree to you as many 'micorwavers' do !
>
> *by Hiroyuki Ozeki*

Collaborators

- Misaki Tanioka (Toho Univ.)
- Kaori Kobayashi (IMS, Toyama Univ.)
- Shuji Saito (IMS)
- Stephane Bailleux (Univ. Lille)
- Georges Wlodarczak (Univ. Lille)

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