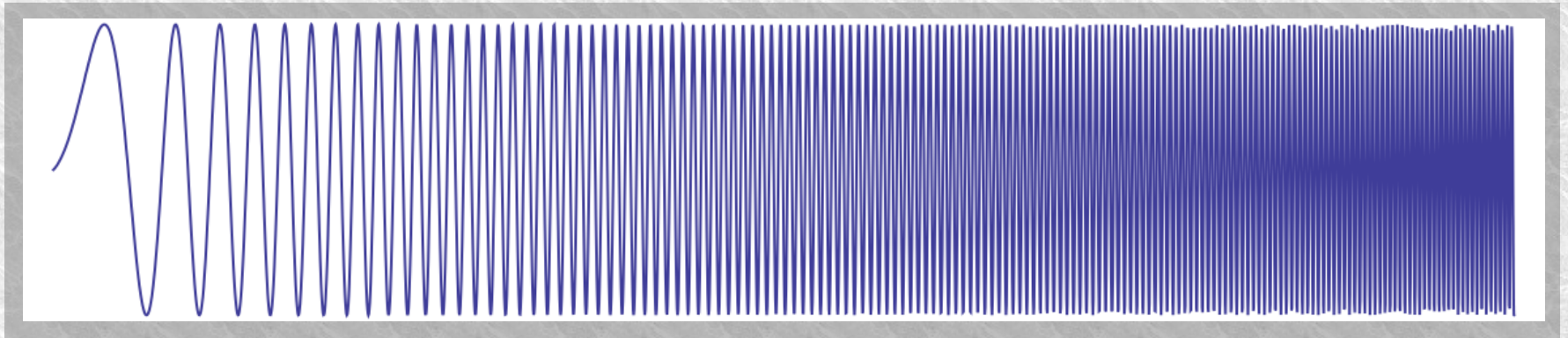# Chirped-Pulse Millimeter-Wave (CPmmW) Spectroscopy
Design and Chemical Application
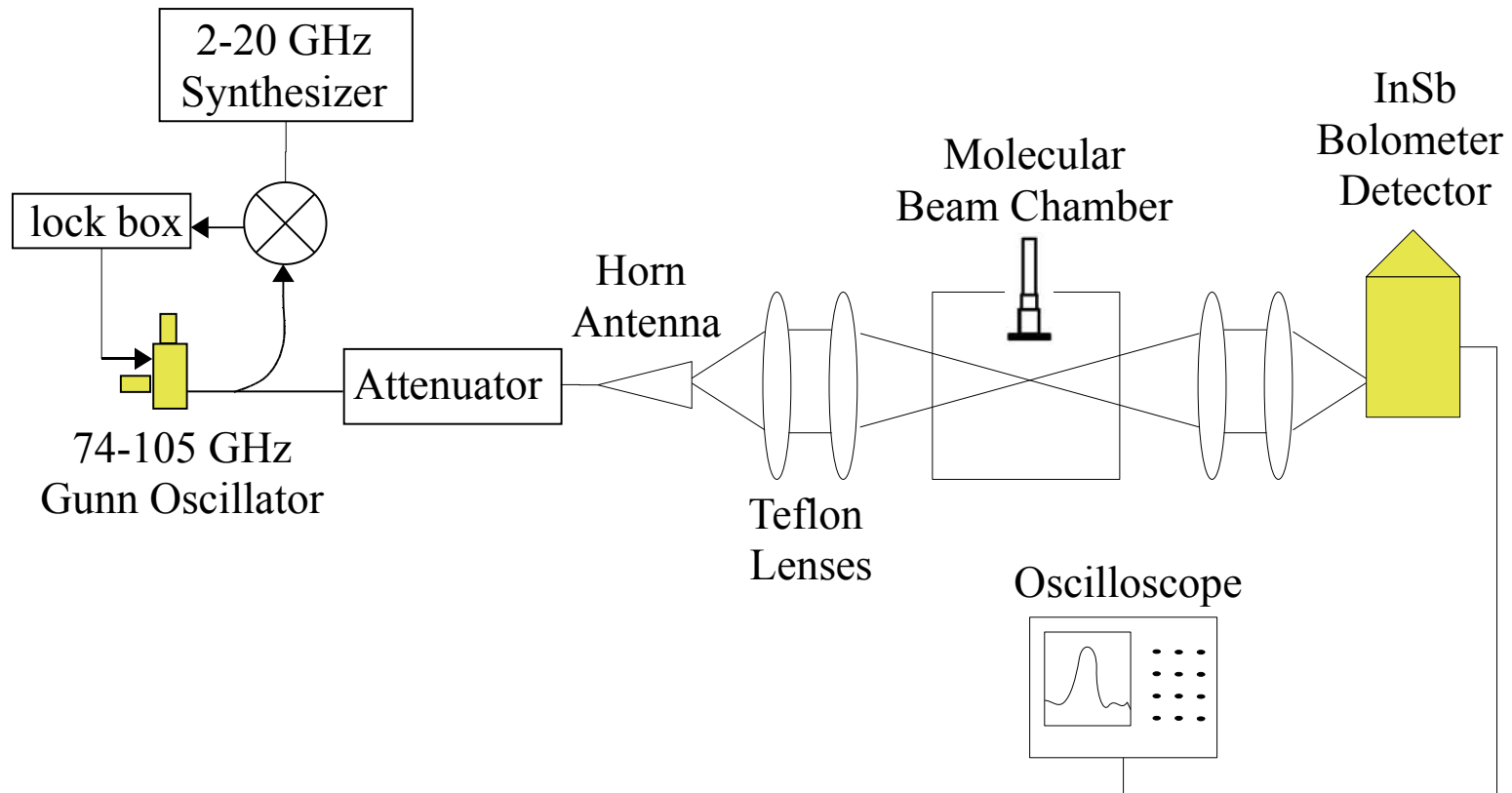

Barratt Park

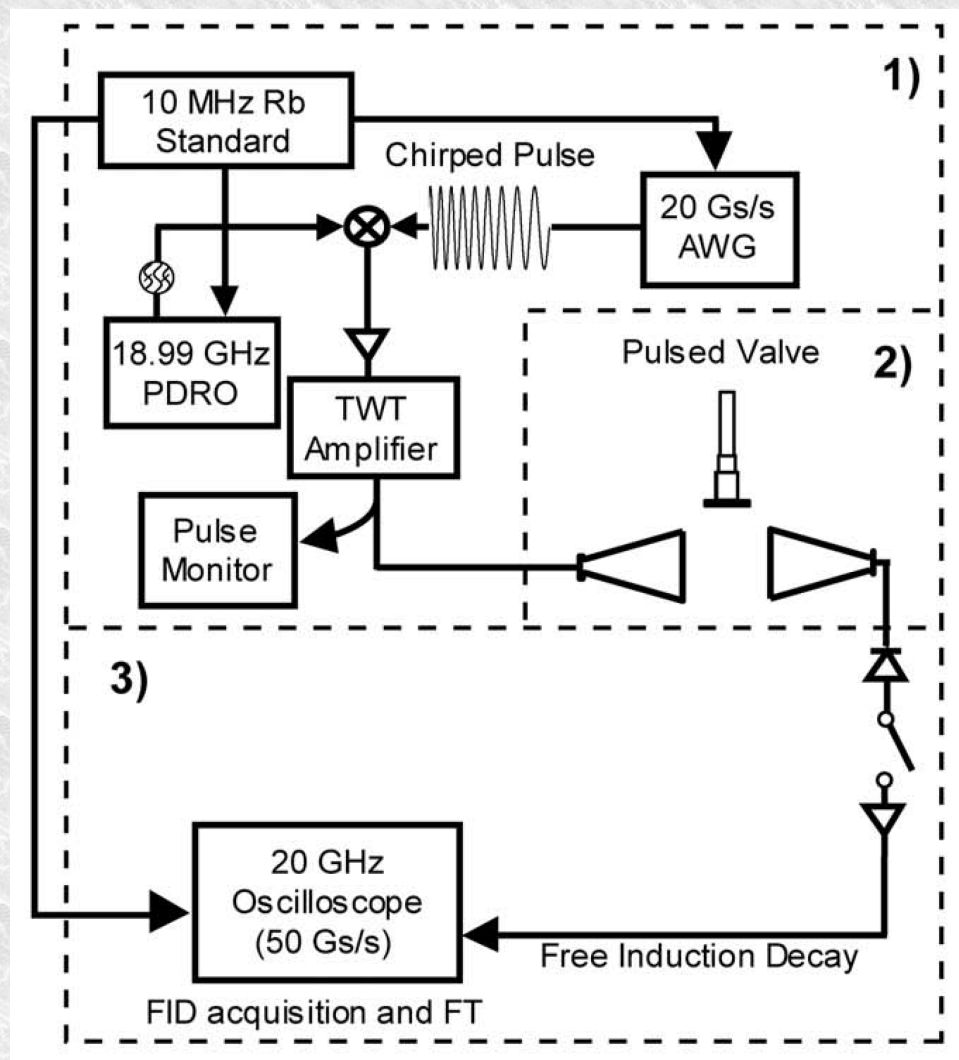Field Group, MIT

Thursday, June 25, 2009

mm-Wave Absorption Spectrometer
Field Lab, 2000

2-20 GHz Synthesizer

lock box

74-105 GHz Gunn Oscillator

Attenuator

Horn Antenna

Teflon Lenses

Molecular Beam Chamber

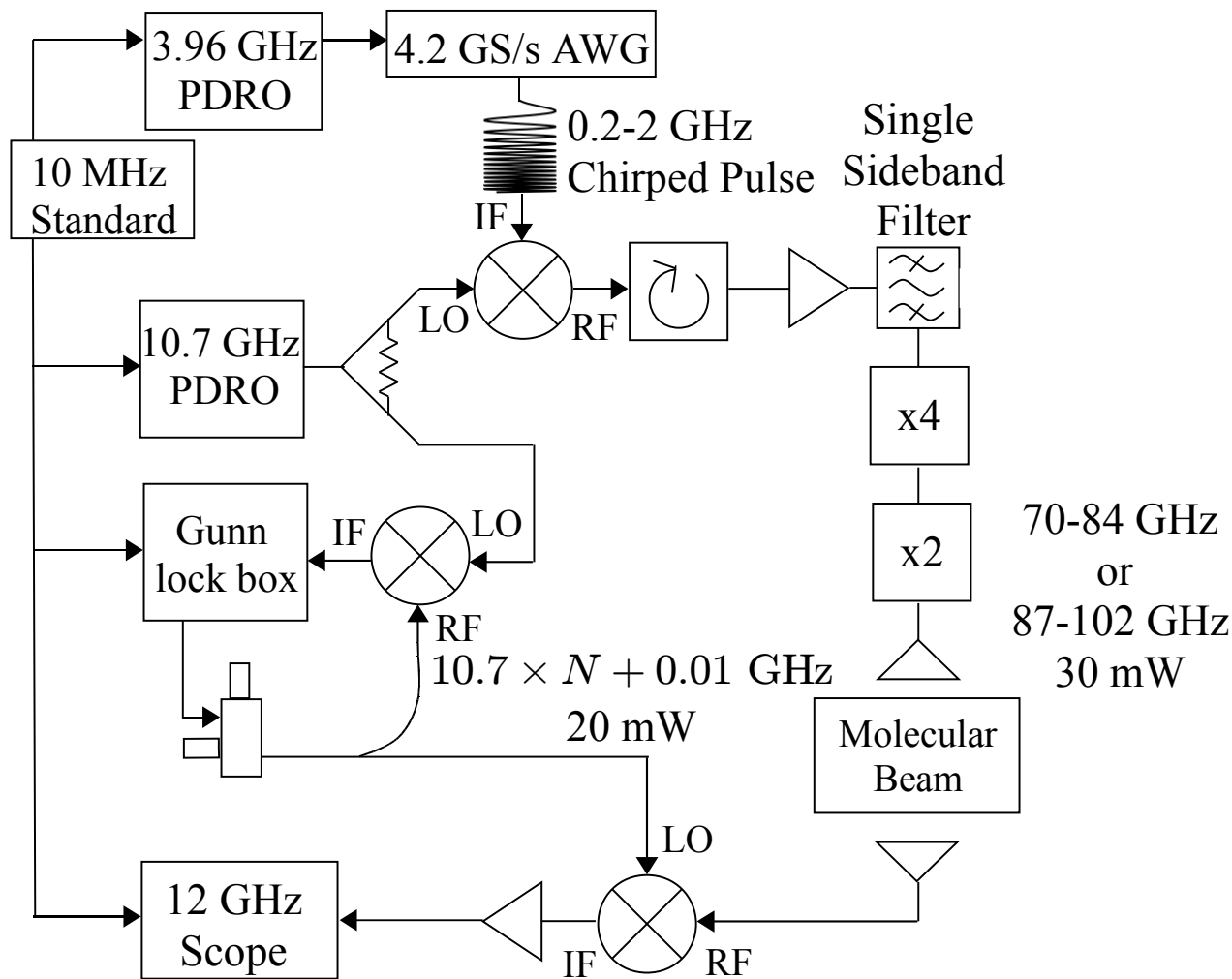InSb Bolometer Detector

Oscilloscope

Pate CPMW Spectrometer

Brown, G. G.; Dian, B. C.; Douglass, K. O.; Geyer, S. M.; Shipman, S. T.; Pate, B. H. *Rev. Sci. Instrum.* **79**, 053103 (2008).

Our CPmmW Spectrometer

Why Use CPmmW?

- Advantages:
  - Broadband Survey Capability at High Resolution
  - Meaningful Relative Intensity Information
- Challenges:
  - Power availability
  - Fast T_2 decay times
  - Achieving phase stability at high frequency

Power Requirements
Single-Frequency Pulse

Assume a typical 1 D transition dipole moment.
Assume power is uniformly focused into a 6.25 cm^2 area.

$$\frac{\pi}{2} = \frac{\mu E t}{\hbar}$$

With 15 dBm, a π/2 pulse should occur at t ≈ 254 ns.

Power Requirements
Single-Frequency Pulse

Assume a typical 1 D transition dipole moment.
Assume power is uniformly focused into a 6.25 cm^2 area.

$$\frac{\pi}{2} = \frac{\mu E t}{\hbar}$$

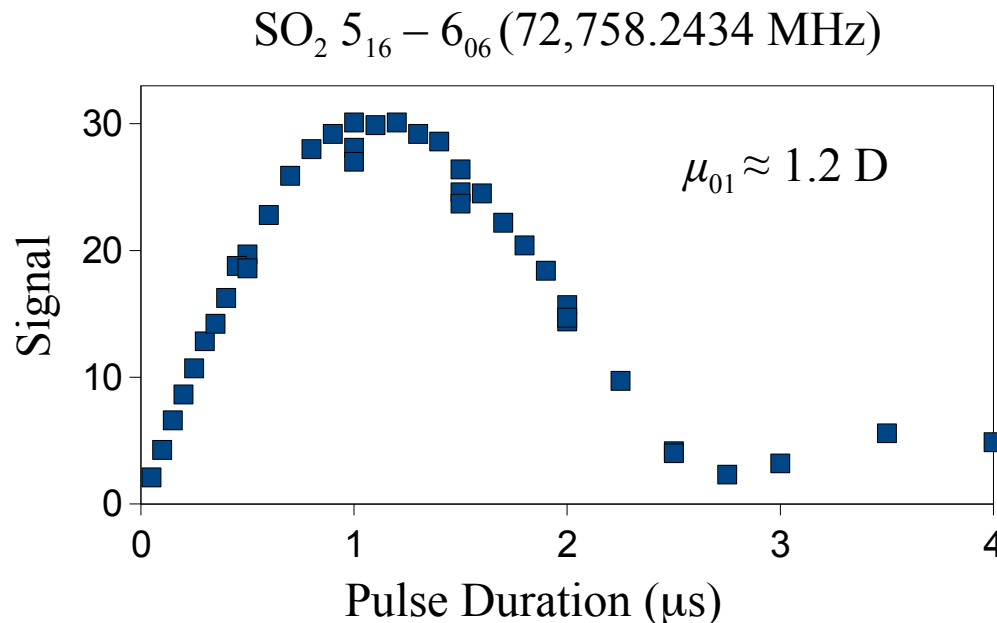With 15 dBm, a $\pi/2$ pulse should occur at t $\approx$ 254 ns.

SO$_2$ $5_{16} - 6_{06}$ (72,758.2434 MHz)

$\mu_{01} \approx 1.2$ D

Signal

Pulse Duration (μs)

Power Requirements
Broadband Pulse

Determine Rabi angle by integration of Bloch equations for the case of a linearly-chirped pulse.

$$P \equiv (P_r + iP_i)e^{i(\omega t - kz)} + \text{c.c.}$$

$$0 = \frac{dP_r}{dt} + \Delta\omega P_i + \frac{P_r}{T_2}$$

$$0 = \frac{dP_i}{dt} - \Delta\omega P_r + |\mu_{ab}|^2 E\left(\frac{\Delta N}{\hbar}\right) + \frac{P_i}{T_2}$$

$$0 = \frac{d}{dt}\left(\frac{\hbar\Delta N}{4}\right) - EP_i + \frac{\hbar}{4}\frac{(\Delta N - \Delta N_0)}{T_1}$$
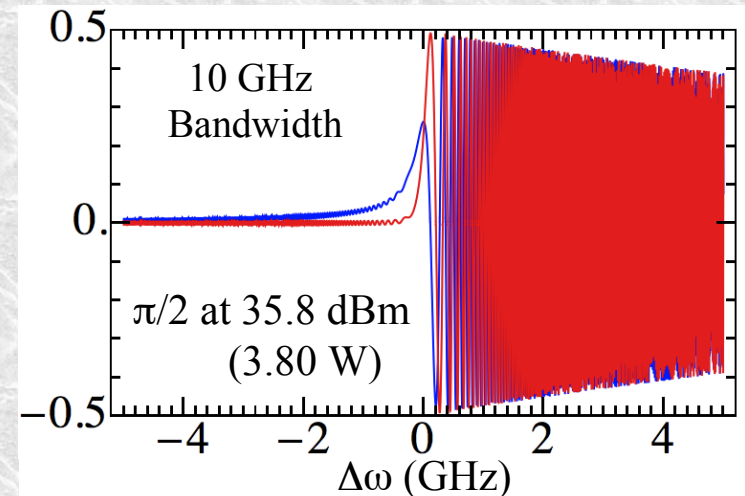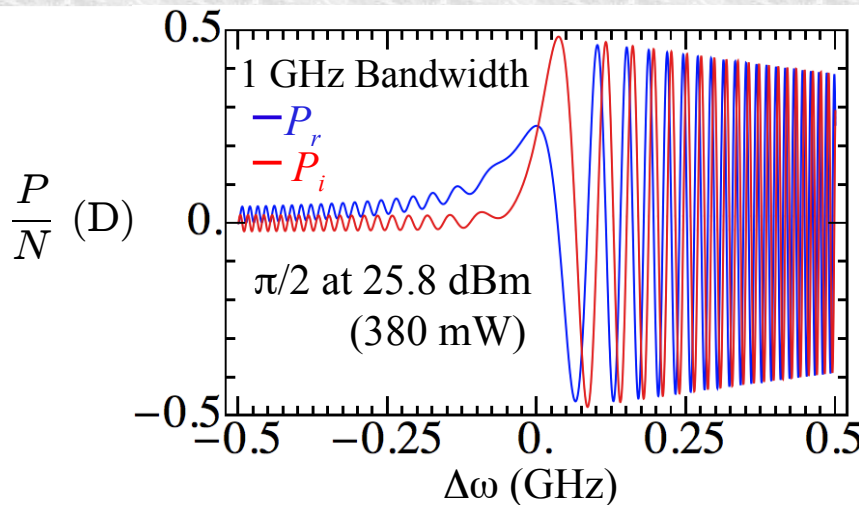
$$\mu_{01} = 1\ \text{D}$$
$$t_{chirp} = 1\ \mu\text{s}$$
$$T_1 = 10\ \mu\text{s}$$
$$T_2 = 2\ \mu\text{s}$$

Assume power is uniformly focused into a 6.25 cm^2 area.

1 GHz Bandwidth
P_r
P_i
$\pi/2$ at 25.8 dBm (380 mW)
$\frac{P}{N}$ (D)
$\Delta\omega$ (GHz)

10 GHz Bandwidth
$\pi/2$ at 35.8 dBm (3.80 W)
$\Delta\omega$ (GHz)

Power Requirements
Broadband Pulse

Determine Rabi angle by integration of Bloch equations for the case of a linearly-chirped pulse.

$$P \equiv (P_r + iP_i)e^{i(\omega t - kz)} + \text{c.c.}$$

$$0 = \frac{dP_r}{dt} + \Delta\omega P_i + \frac{P_r}{T_2}$$

$$0 = \frac{dP_i}{dt} - \Delta\omega P_r + |\mu_{ab}|^2 E\left(\frac{\Delta N}{\hbar}\right) + \frac{P_i}{T_2}$$

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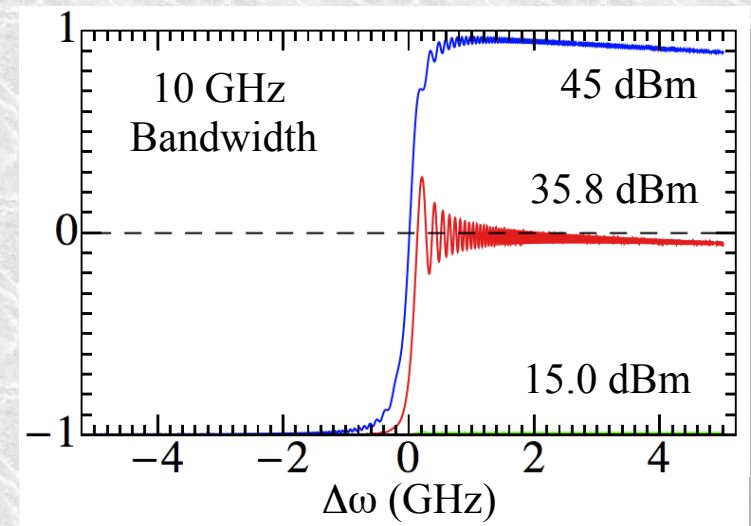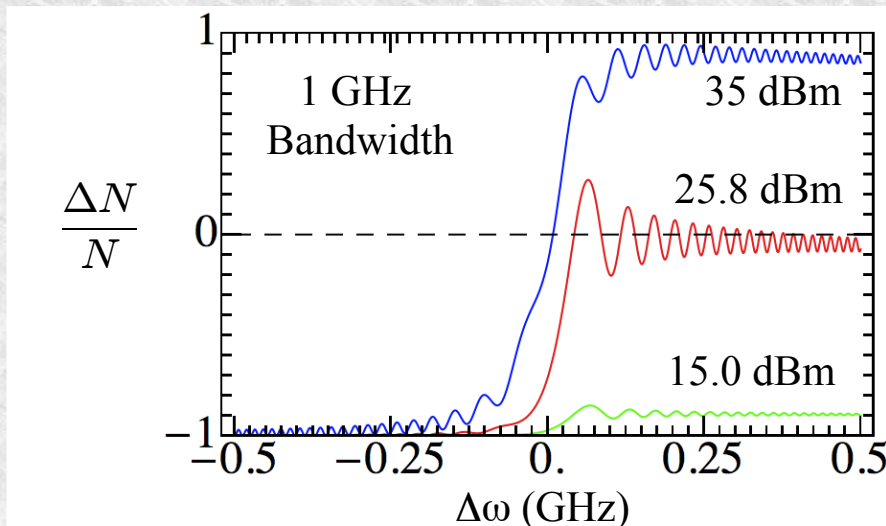
$$\mu_{01} = 1 \text{ D}$$
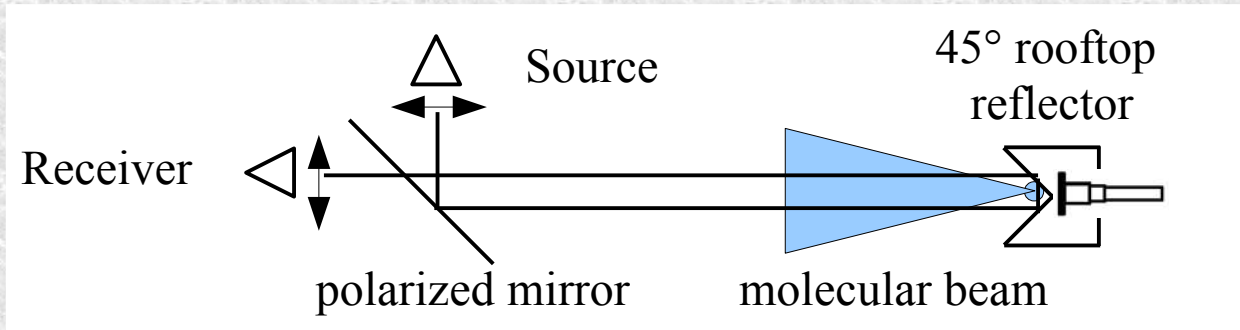$$t_{chirp} = 1 \ \mu\text{s}$$
$$T_1 = 10 \ \mu\text{s}$$
$$T_2 = 2 \ \mu\text{s}$$

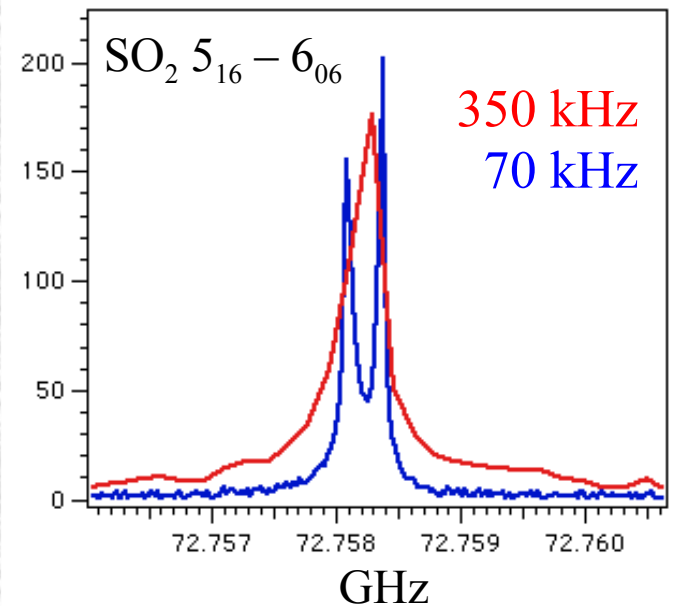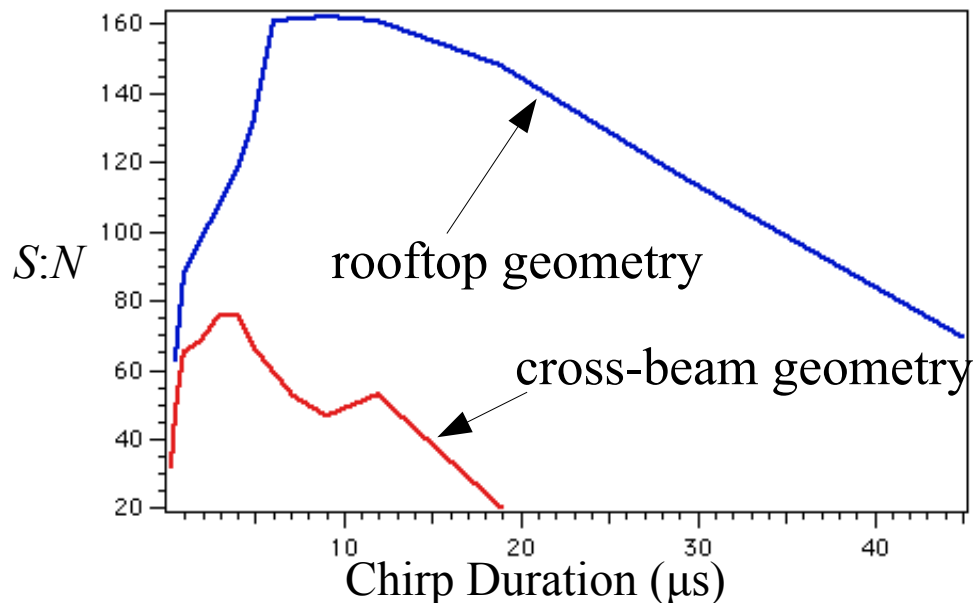Assume power is uniformly focused into a 6.25 cm^2 area.

Overcoming Fast T_2 Decay
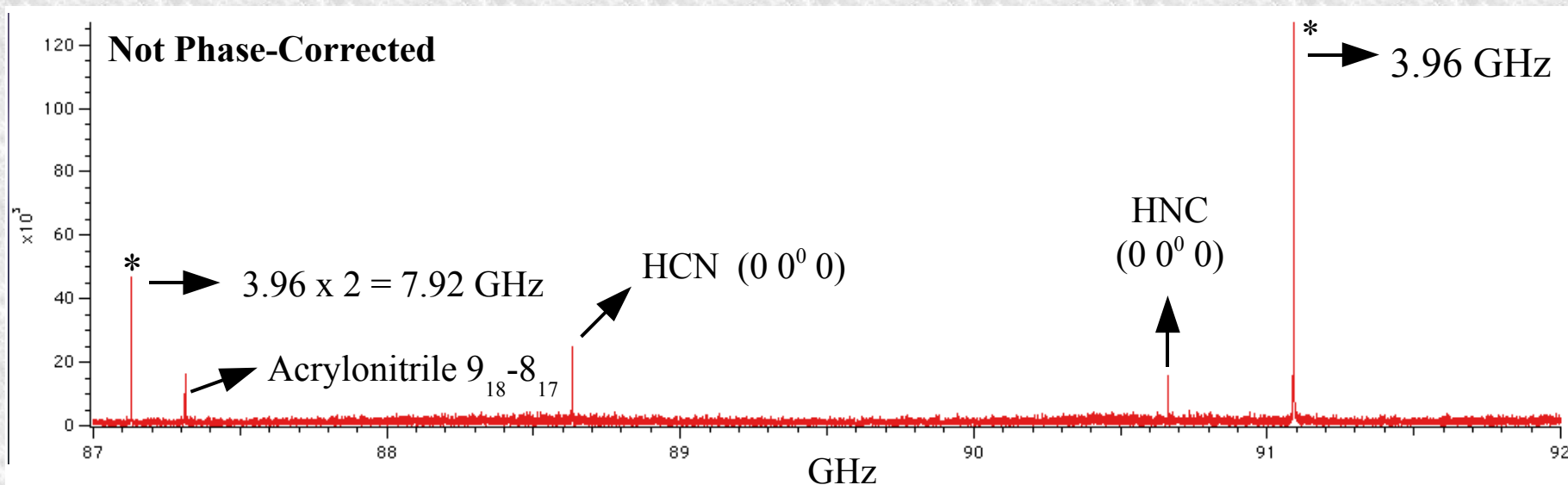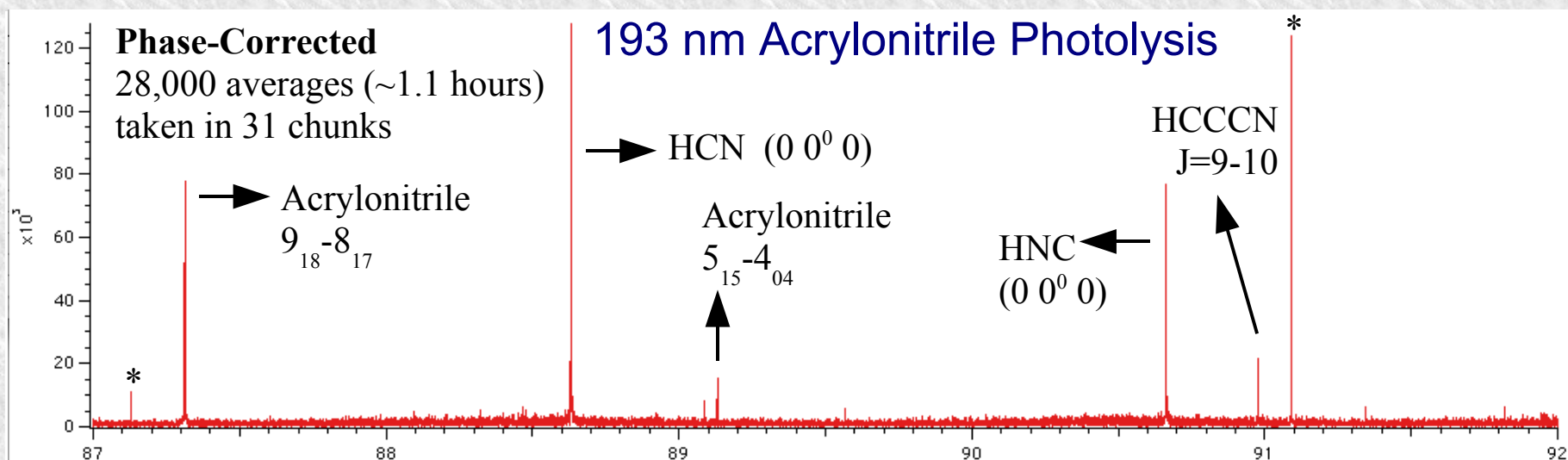## Reduction of Doppler Broadening

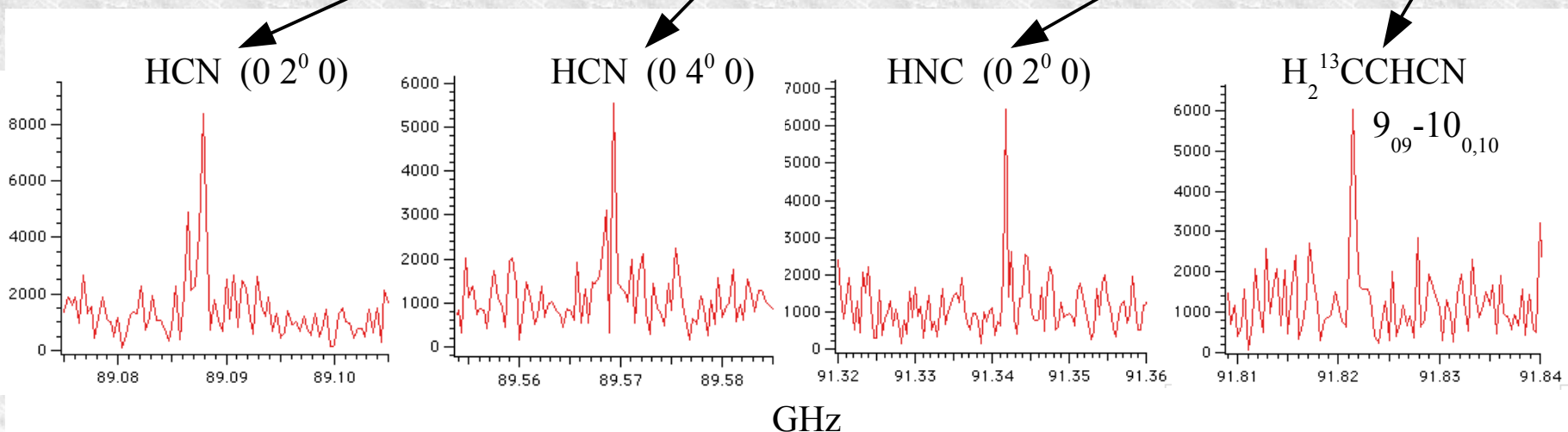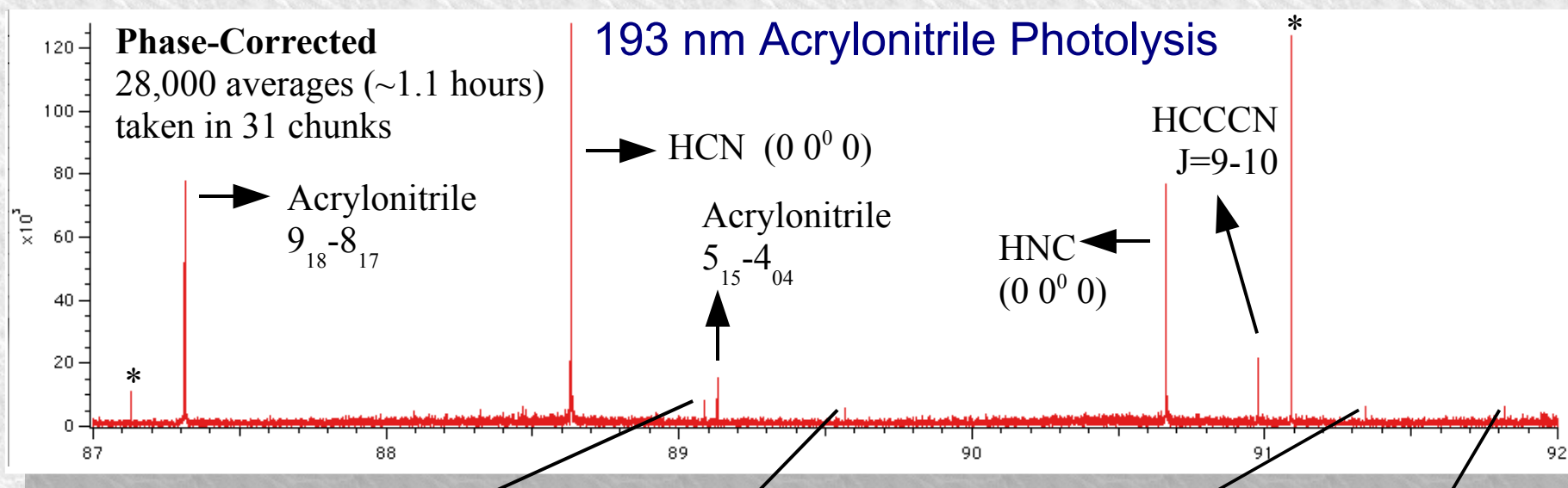1 GHz Bandwidth chirped pulse centered around transition

Phase Correction

- Long-term phase drift can be corrected in signal processing.
  - Collect a series of short acquisitions (~1000 avg)
  - Take the FT (real and imaginary parts)
  - Rotate the phase of each spectrum to maximize overlap of a strong line.
  - Average the FT's

Phase Correction

Phase-Corrected
28,000 averages (~1.1 hours)
taken in 31 chunks

193 nm Acrylonitrile Photolysis

HCN $(0\,0^0\,0)$

Acrylonitrile
$9_{18}\text{-}8_{17}$

Acrylonitrile
$5_{15}\text{-}4_{04}$

HCCCN
J=9-10

HNC
$(0\,0^0\,0)$

Not Phase-Corrected

3.96 GHz

3.96 x 2 = 7.92 GHz

HCN $(0\,0^0\,0)$

HNC
$(0\,0^0\,0)$

Acrylonitrile $9_{18}\text{-}8_{17}$

GHz

Phase Correction

Phase-Corrected
28,000 averages (~1.1 hours)
taken in 31 chunks

193 nm Acrylonitrile Photolysis

HCN $(0\ 0^0\ 0)$

Acrylonitrile 9_{18}-8_{17}

Acrylonitrile 5_{15}-4_{04}

HCCCN J=9-10

HNC $(0\ 0^0\ 0)$

HCN $(0\ 2^0\ 0)$

HCN $(0\ 4^0\ 0)$

HNC $(0\ 2^0\ 0)$

$H_2^{13}CCHCN$ 9_{09}-$10_{0,10}$

GHz

Bolometer-Detected Absorption

Bandwidth = 100 MHz
S:N = 670
Acquisition Time = 100 min.

OCS (J = 6-5)

Chirped Pulse

OC^{34}S

x 60

O^{13}CS

OCS (v_2 = 1)

Bandwidth = 4 GHz
S:N = 1500
Acq. Time = 50 min.

GHz

Survey Mode

OCS ($J = 6$-5)

100 Avg.
30 sec
S:N = 220

1000 Avg.
5 min
S:N = 580

10,000 Avg.
50 min
S:N = 1500

GHz
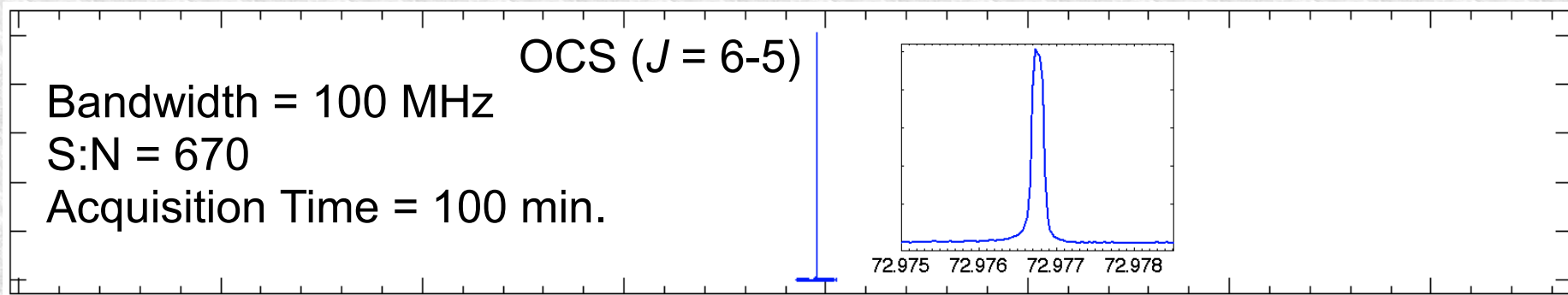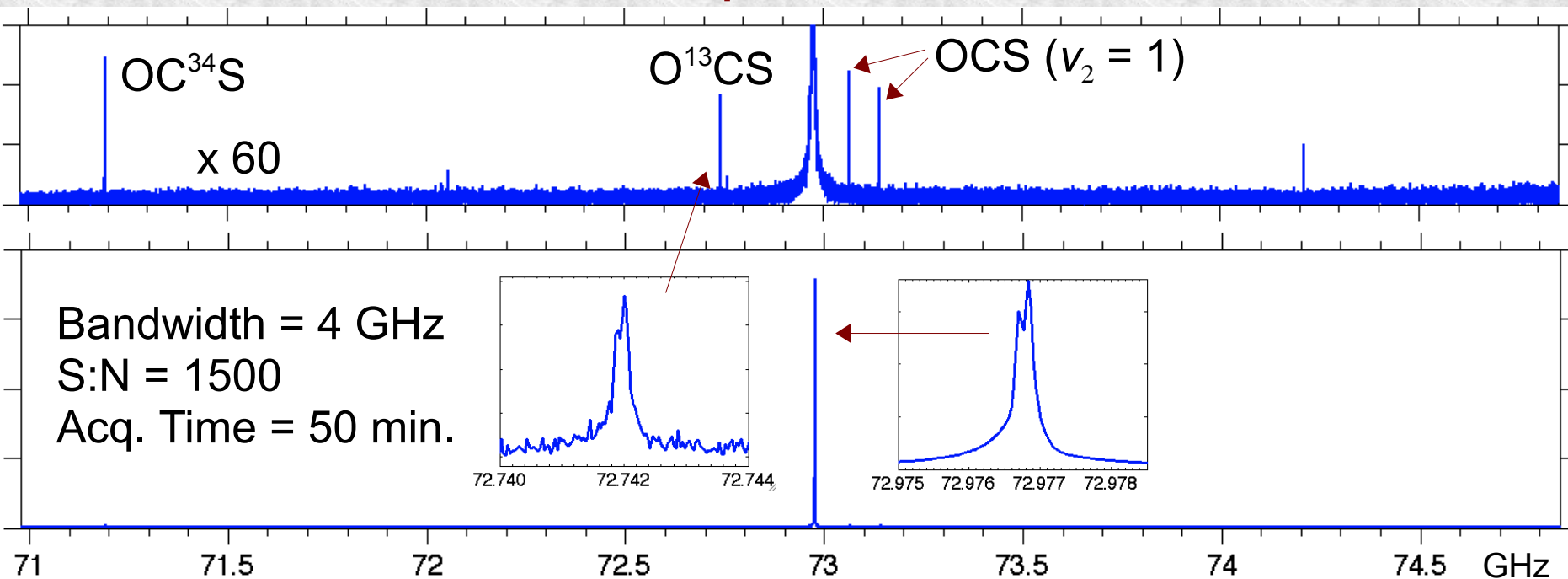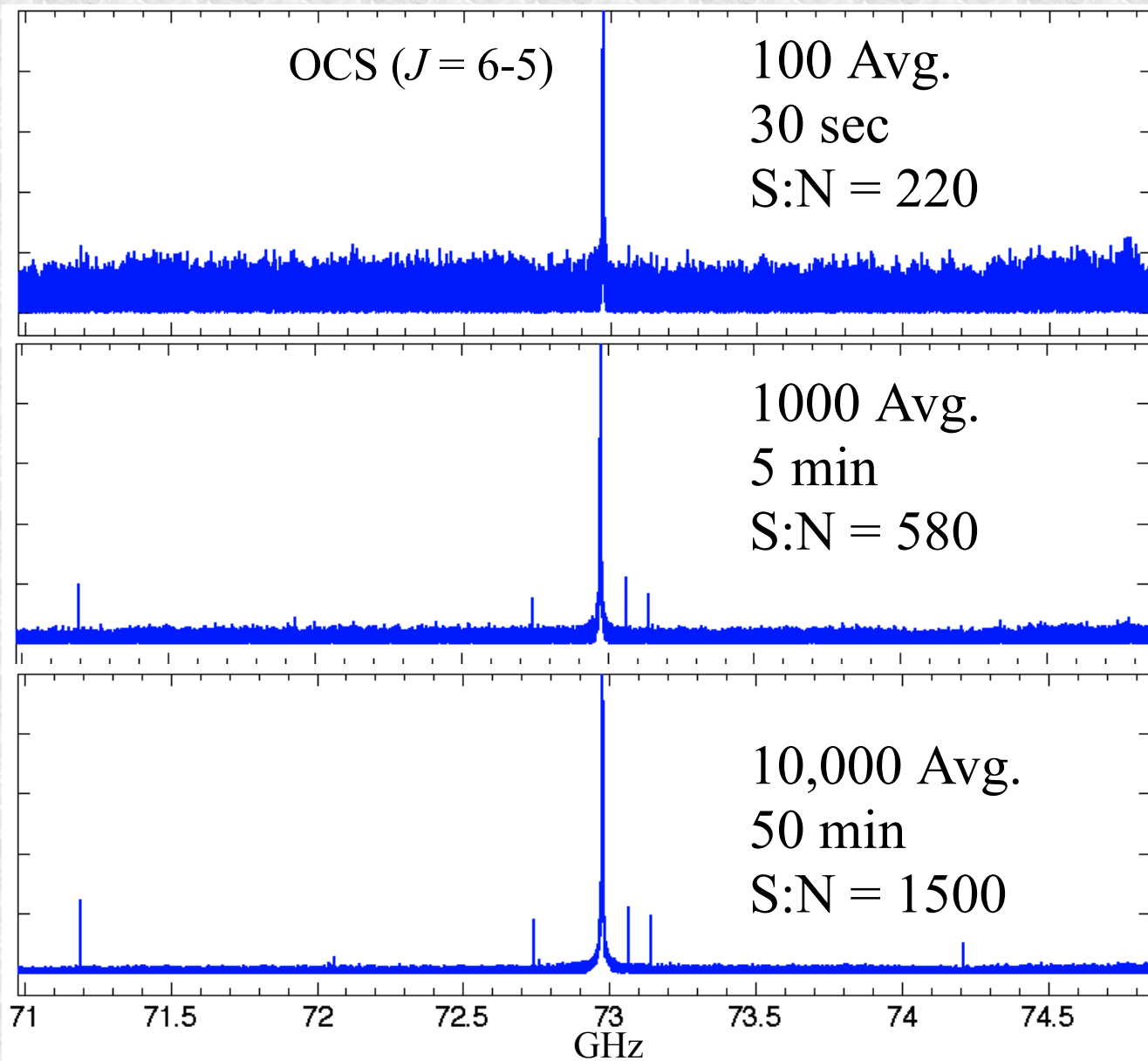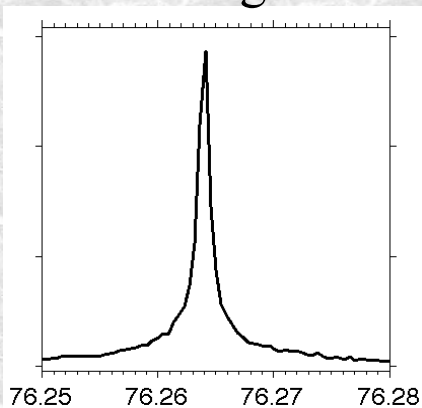
Laser-CPmmW Double Resonance

500 ns FT-limited pulse
1000 averages

Dye Laser:
CS $e\,{}^3\Sigma^-$ - $X\,{}^1\Sigma^+$ (v = 2-0)
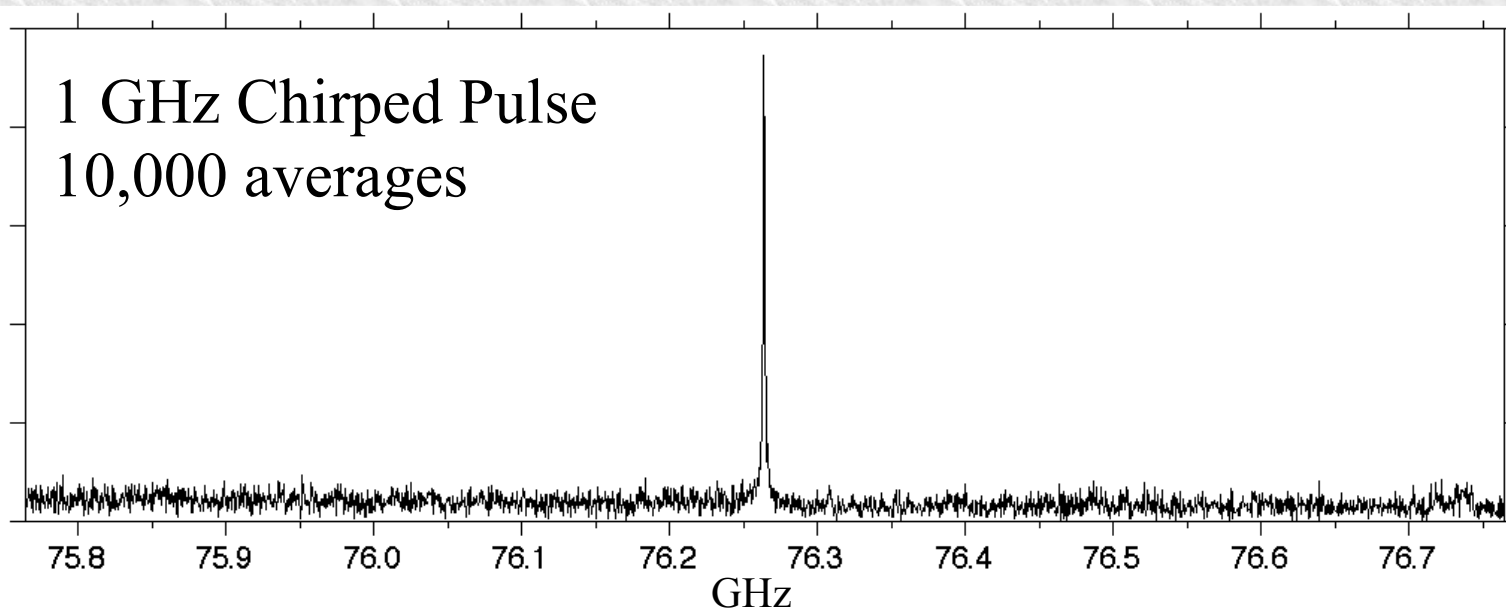$Q(1)$ = 40065.5 cm^{-1}

mm-Waves:
J' = 2, N' = 2 – J' = 1, N' = 1
76.264 GHz

1 GHz Chirped Pulse
10,000 averages

GHz

Acknowledgements

Our CPmmW Spectrometer
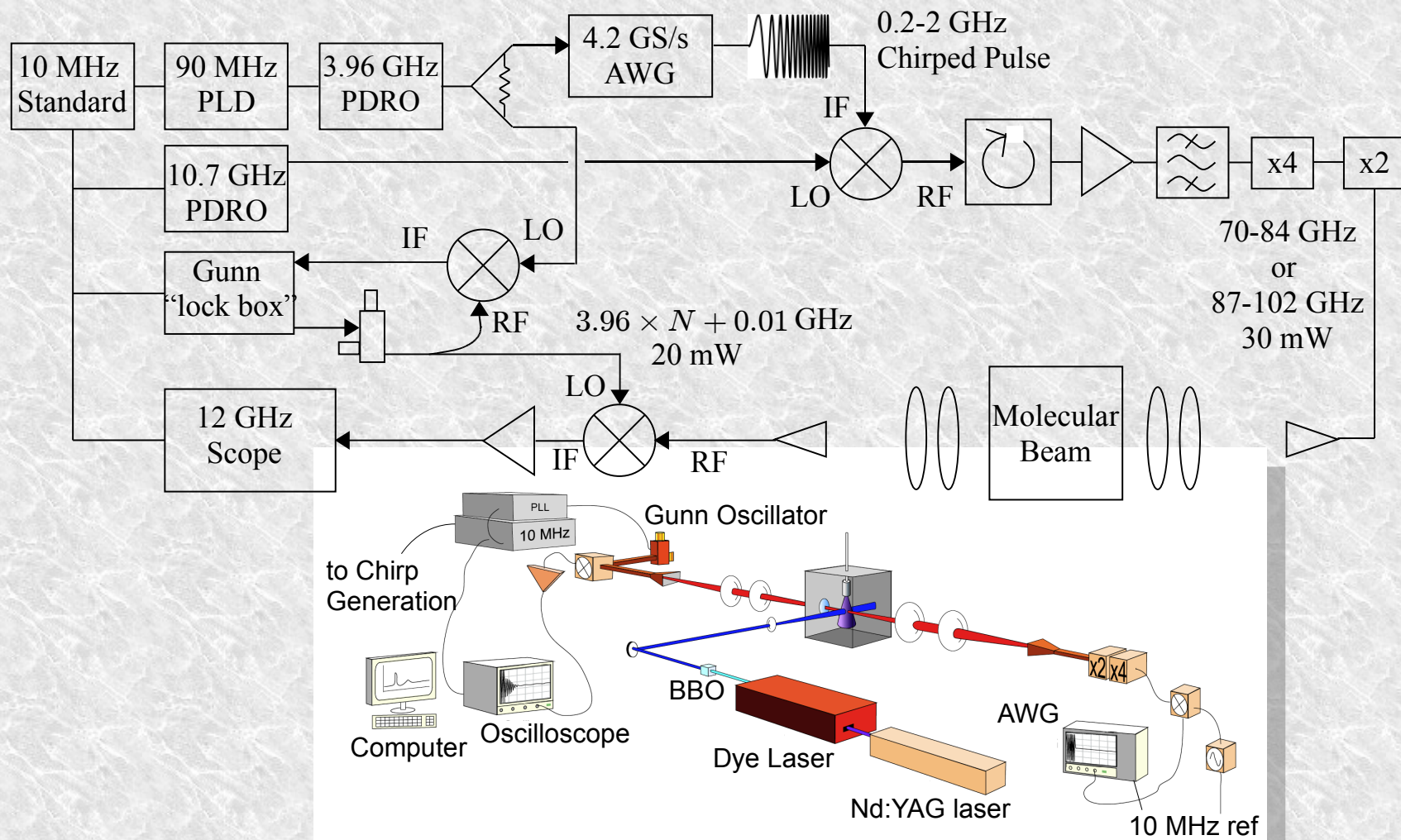
Power Requirements
Single-Frequency Pulse

$SO_2 \ 5_{16} - 6_{06} \ (72{,}758.2434 \ \text{MHz})$
Signal vs. E-Field
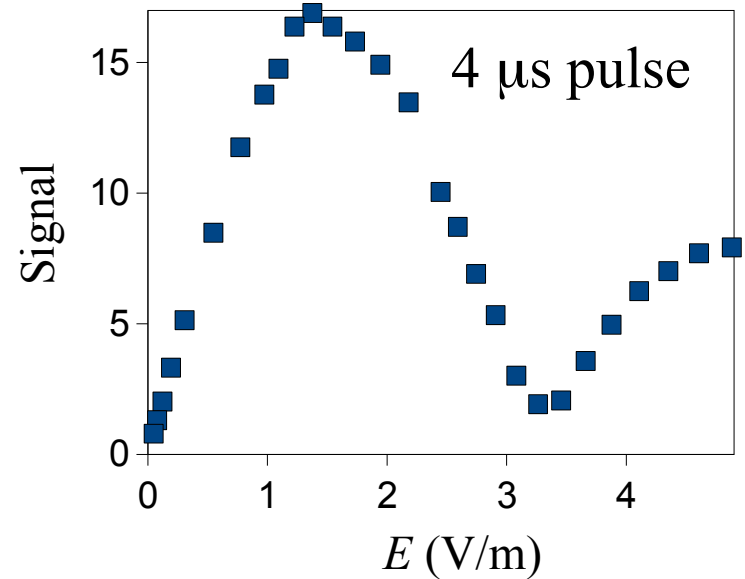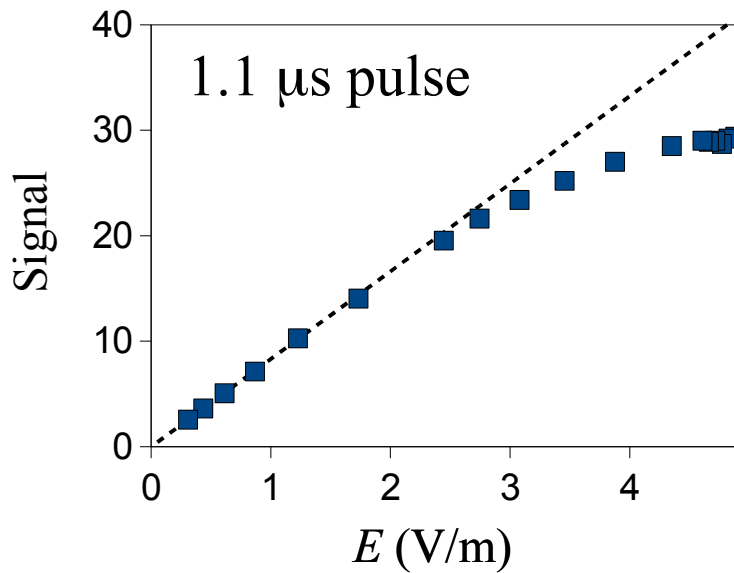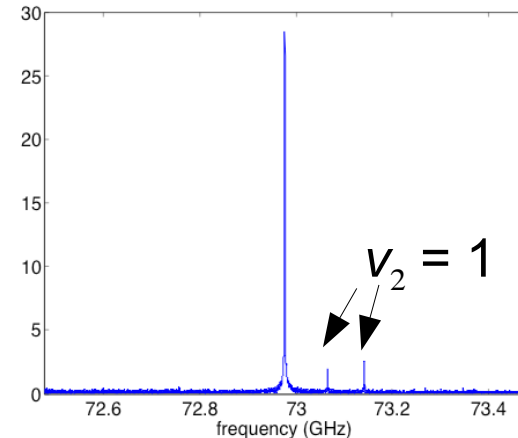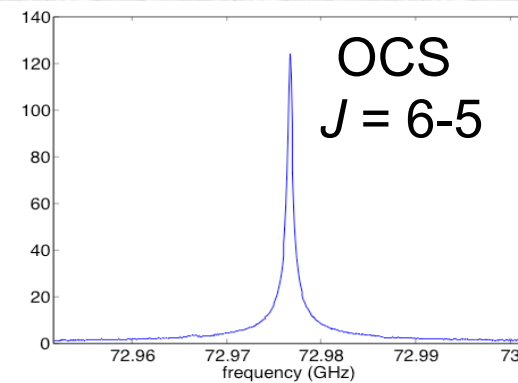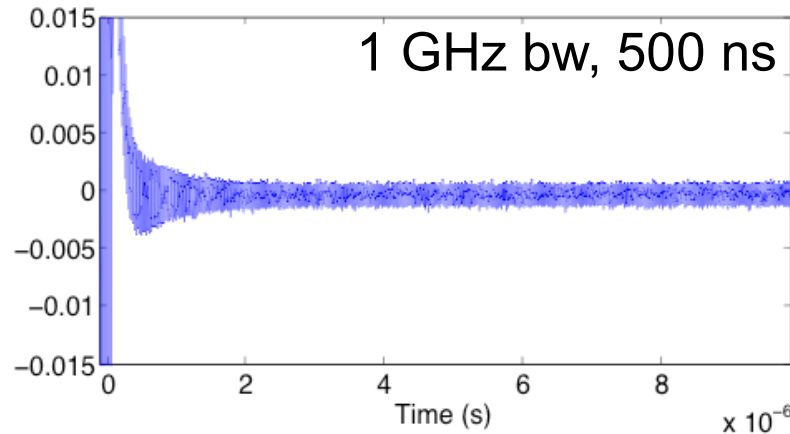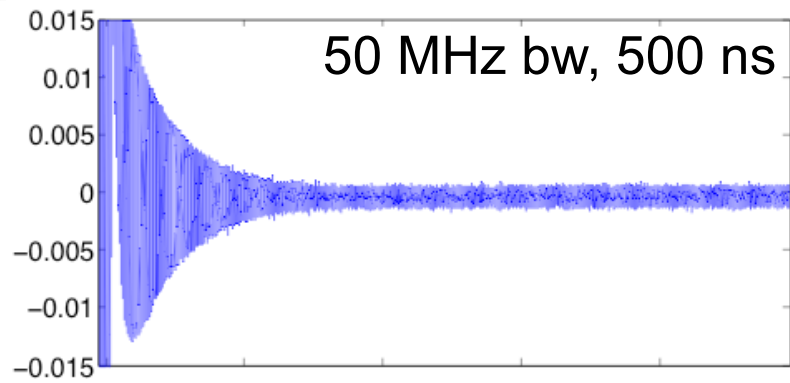
Signal Strength vs. Bandwidth

Ratio of $\frac{1}{\sqrt{\Delta\nu}} = \sqrt{\frac{1000}{50}} = 4.5$

Ratio of Signal Intensity = 4.15

Conclusion: we are within ~8% of the ideal signal scaling $P \propto \frac{|\mu_{ab}|^2 E_0 \Delta N_0}{\hbar} \left(\frac{\pi\tau}{\Delta\nu}\right)^{1/2}$

Line Intensity vs. E Field

Acetonitrile 73588.86 MHz line, 10 MHz sweep

Linearity implies low power limit.
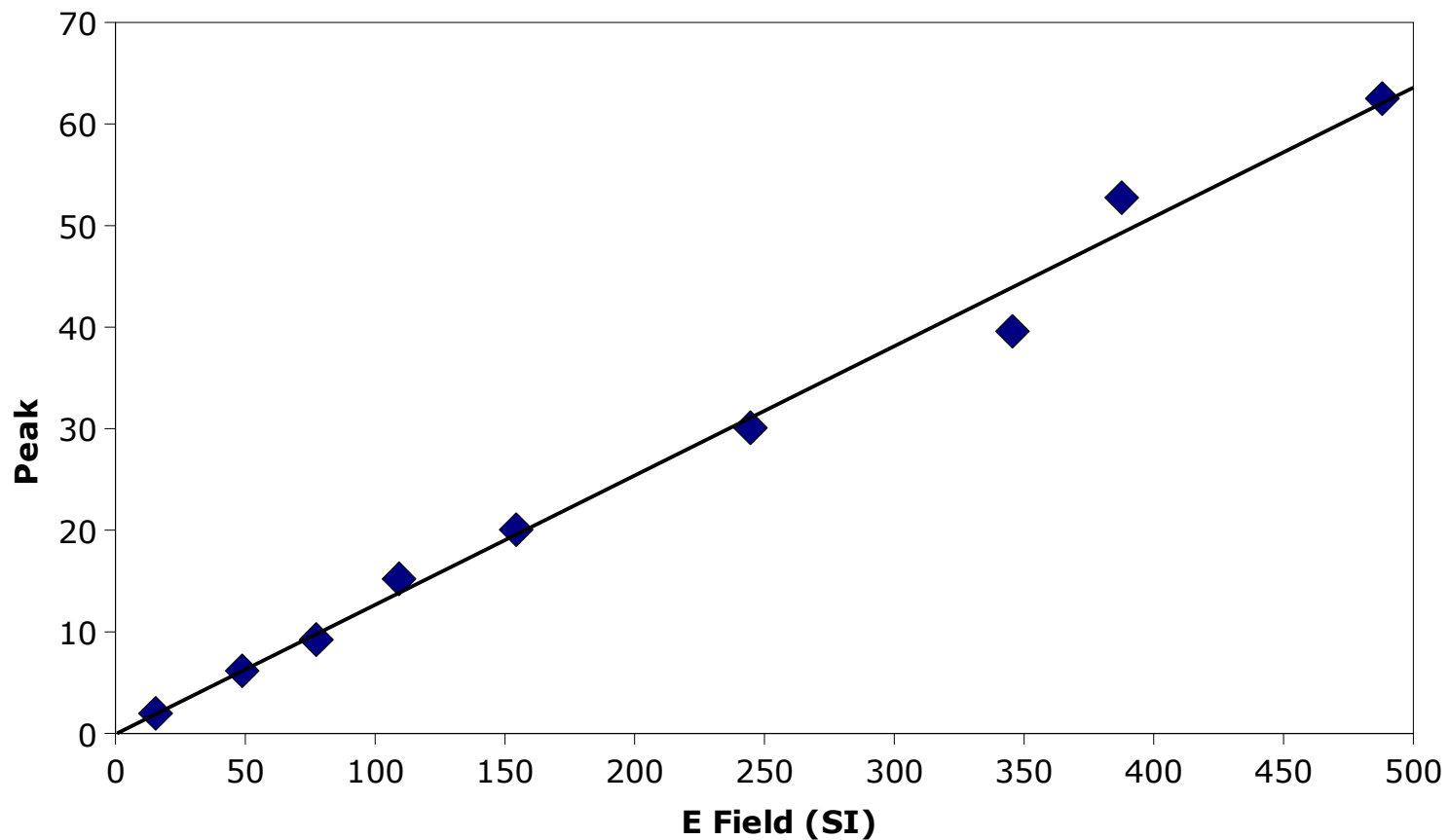
OCS *J* = 6-5 Pressure Broadening
A Lesson in Lifetime

- 0.500 μs chirp duration
- 20 μs FID collection time
- Pressure broadening is ~20 MHz / torr
- Signal drops when τ < chirp duration

P_{OCS} (mtorr)	FWHM (kHz)	Decay Time (τ) (μs)
3.5	262 ± 3	2.11 ± 0.03
20	780 ± 3	0.707 ± 0.003
100	2507 ± 5	0.2199 ± 0.0004

$$g(\omega) = \frac{A}{\sqrt{\Gamma^2 + (\omega_0 - \omega)^2}}$$

$$FWHM = 2\sqrt{3}\Gamma$$

$$\tau = \frac{T_1 T_2}{T_1 + T_2} = \frac{1}{2\pi\Gamma}$$
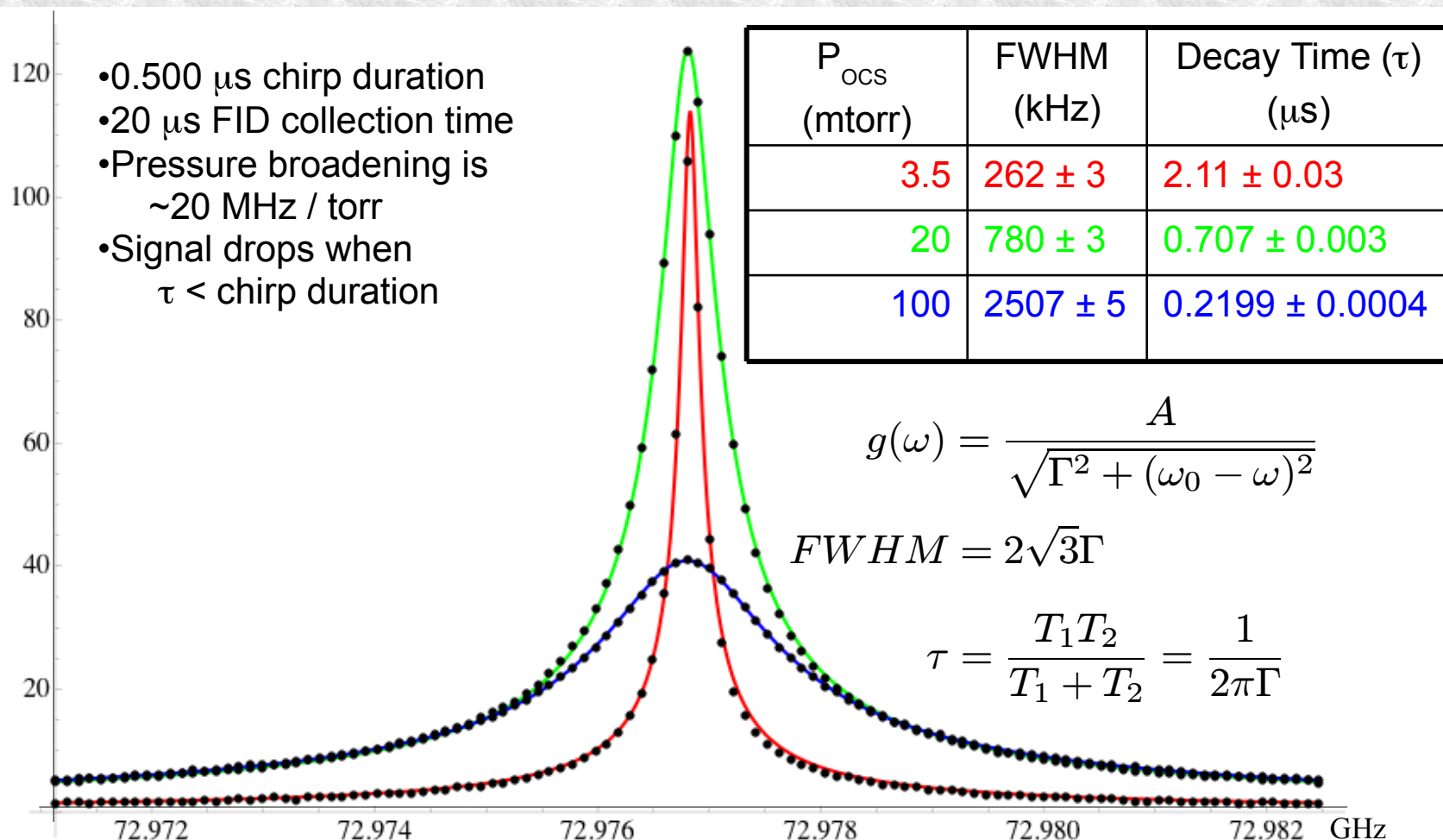
Acrylonitrile Photolysis

Nascent Vibrational State Distribution:

An ideal nail for the CPmmW hammer

$$\text{Acrylonitrile} \xrightarrow{\text{193 nm}} \text{Products}$$

- The mechanism for 193 nm photolysis of acrylonitrile—particularly the HCN, HNC channel--is a subject of hot controversy.

- Vibrational levels of HCN and HNC have J = 1-0 transitions between 87-92 GHz. Can record all lines at once.

- Accurate intensity information can be put to use.

- Product distribution may elucidate mechanism.

C_2H_3CN Fragmentation in Electric Discharge
5 GHz Bandwidth, 500 averages (1 minute acquisition time)
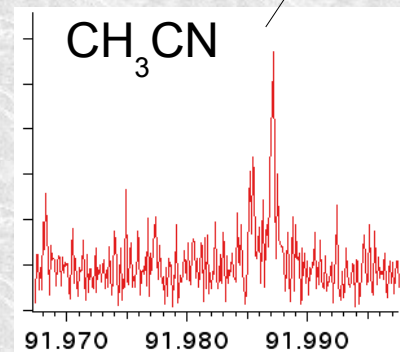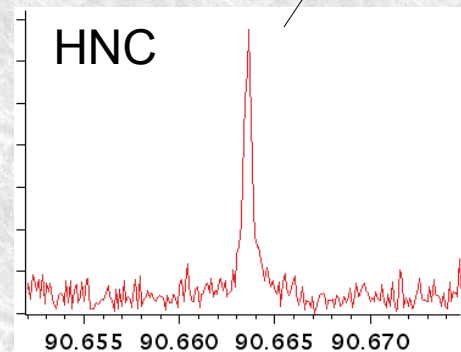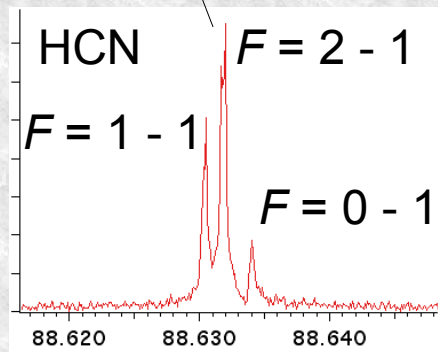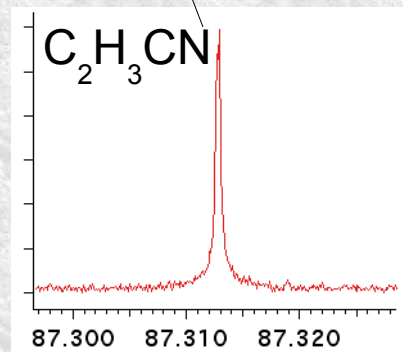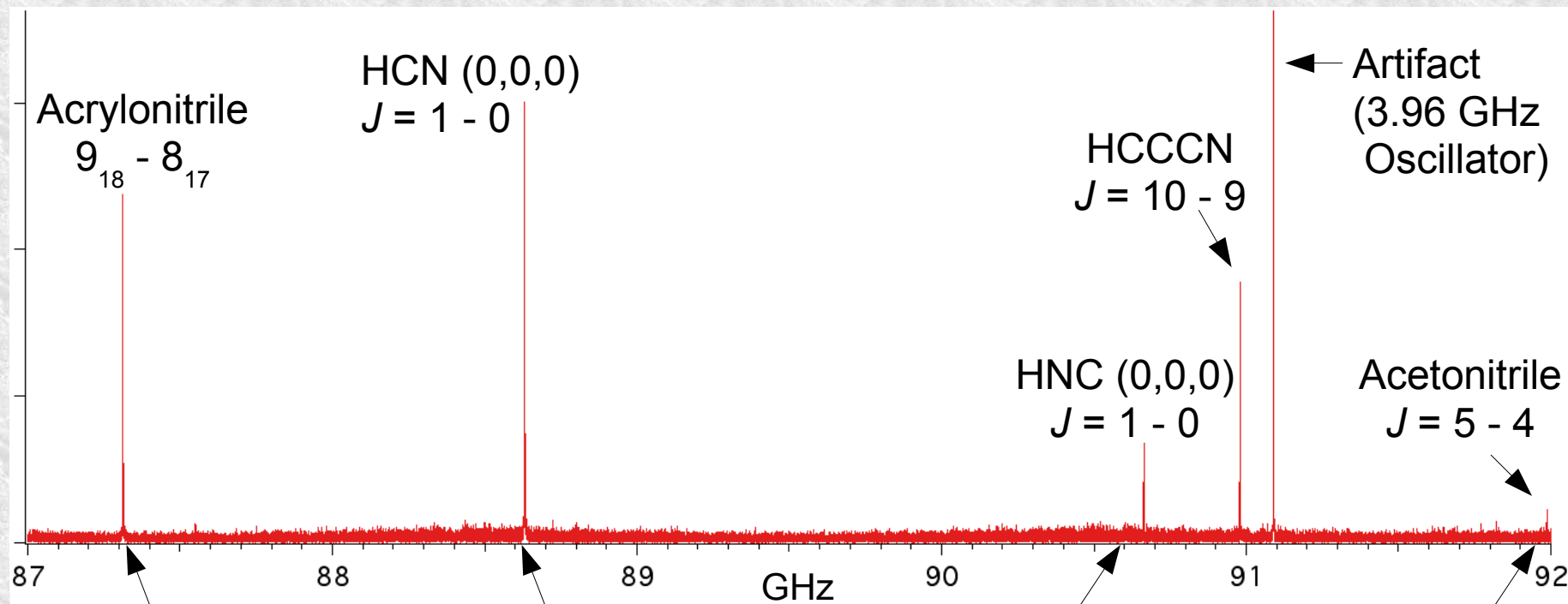
Millimeter Waves

Electronics   Optics

Radio   Microwaves   Infrared   Ultraviolet   X-Ray   Gamma Ray

λ (m) 10^3 10^{-2} 10^{-3} 10^{-5} 10^{-6} 10^{-8} 10^{-10} 10^{-12}

ν (s^{-1}) 10^4 10^8 10^{10} 10^{12} 10^{13} 10^{15} 10^{18} 10^{20}
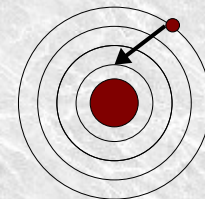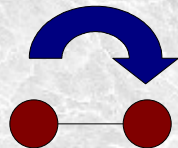
Millimeter Waves

High resolution makes millimeter waves an effective probe of electronic properties.

Bechtel, H.A.; Steeves, A. H.; Wong, B. M.; Field, R. W. *Angew. Chem. Int. Ed.*, **47**, 2969 (2008).

The Balle-Flygare
FT Microwave Spectrometer

Balle, T. J.; Campbell, E. J.; Keenan, M. R.; Flygare, W. H. *J. Chem. Phys.*, **71**, 2723 (1979).

Signal Scaling with Bandwidth

FT-Limited Pulse

$$\psi = a|a\rangle + b|b\rangle$$

$$|ab| = \sin\left(\frac{\mu_{ab}E\tau_c}{\hbar}\right) \approx \frac{\mu_{ab}E\tau_c}{\hbar}$$

$$P = N\langle\mu\rangle = N\mathrm{Tr}[\rho\mu]$$
$$= N(ab\,\mu_{ab} + \mathrm{c.c.})$$
$$|P| \approx N|\mu_{ab}|^2 E\tau_c/\hbar$$
$$= \frac{|\mu_{ab}|^2 EN}{2\pi\hbar\Delta\nu_c}$$

Chirped Pulse

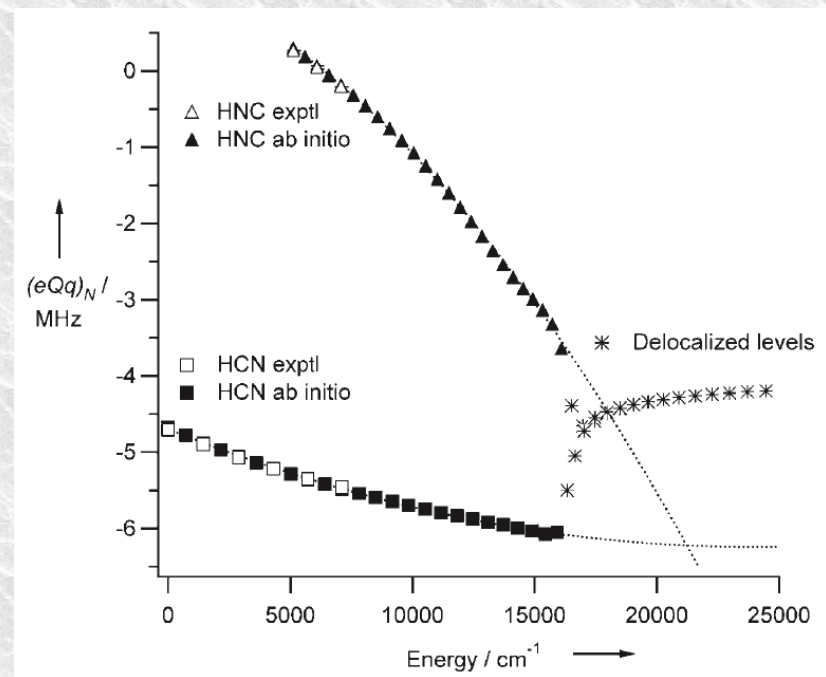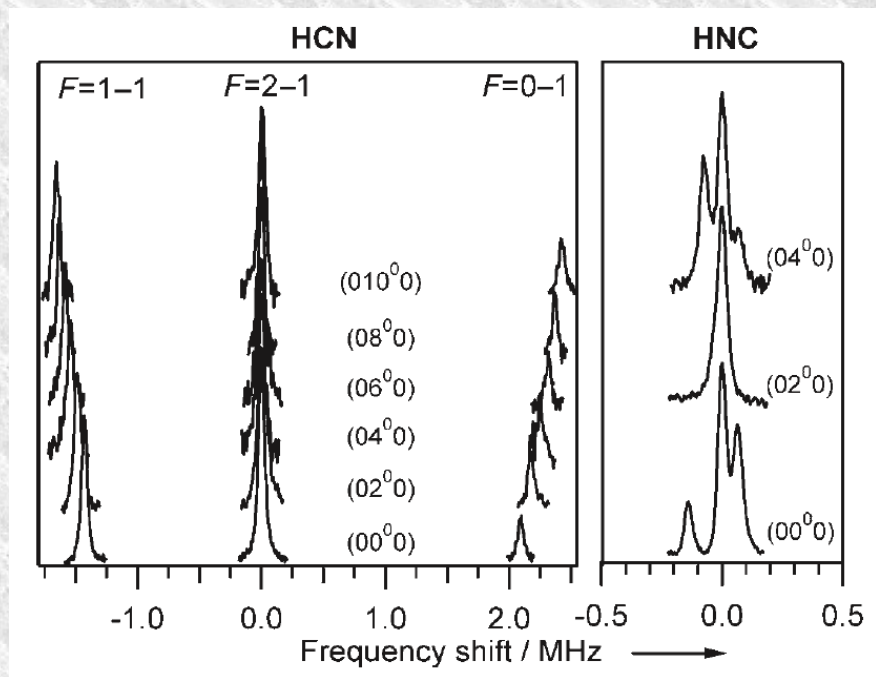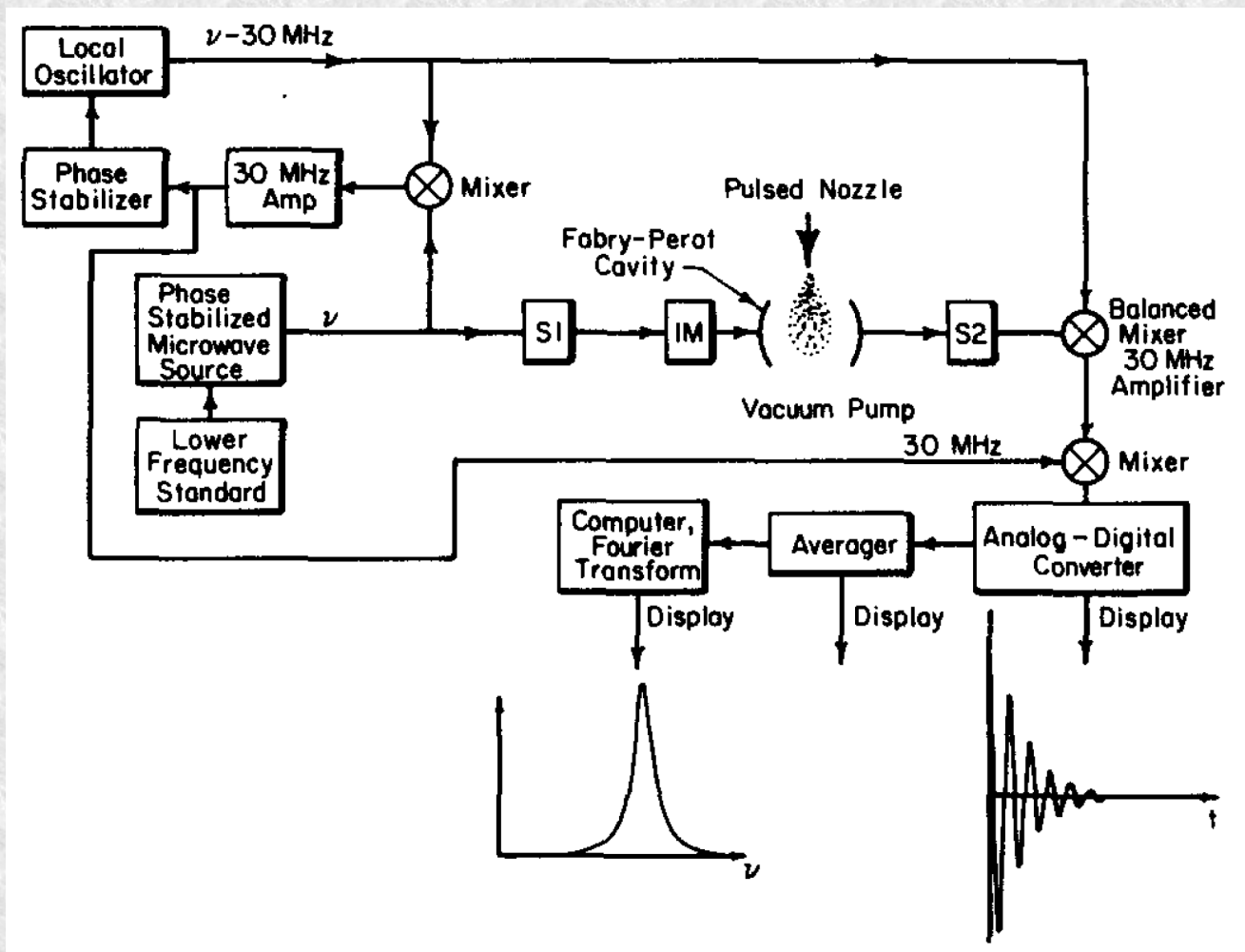McGurk, J. C.; Schmalz, T. G.; Flygare, W. H.
J. Chem. Phys. **60**, 4181, (1974).

Direct integration of Bloch Equations

$$0 = \frac{dP_r}{dt} + \Delta\omega P_i + \frac{P_r}{T_2}$$

$$0 = \frac{dP_i}{dt} - \Delta\omega P_r + |\mu_{ab}|^2 E\left(\frac{\Delta N}{\hbar}\right) + \frac{P_i}{T_2}$$

$$0 = \frac{d}{dt}\left(\frac{\hbar\Delta N}{4}\right) - EP_i + \frac{\hbar}{4}\frac{(\Delta N - \Delta N_0)}{T_1}$$

Assume   1. Population Transfer is Small
2. No Decay

$$0 = \alpha\frac{dP_r}{d\Delta\omega} + \Delta\omega P_i$$

$$0 = \alpha\frac{dP_i}{d\Delta\omega} - \Delta\omega P_r + |\mu_{ab}|^2 E\left(\frac{\Delta N_0}{\hbar}\right)$$

$$P_r(\Delta\omega_f) = \frac{|\mu_{ab}|^2 E}{\hbar}\Delta N_0\left(\frac{\pi\tau}{\Delta\nu}\right)^{1/2}\left\{\sin\left(\frac{(\Delta\omega_f)^2}{2\alpha}\right)\left[\pm C\left|\frac{\Delta\omega_i}{(\pi\alpha)^{1/2}}\right| \pm C\left|\frac{\Delta\omega_f}{(\pi\alpha)^{1/2}}\right|\right] - \cos\left(\frac{(\Delta\omega_f)^2}{2\alpha}\right)\left[\pm S\left|\frac{\Delta\omega_i}{(\pi\alpha)^{1/2}}\right| \pm S\left|\frac{\Delta\omega_f}{(\pi\alpha)^{1/2}}\right|\right]\right\}$$

$$P_i(\Delta\omega_f) = -\frac{|\mu_{ab}|^2 E}{\hbar}\Delta N_0\left(\frac{\pi\tau}{\Delta\nu}\right)^{1/2}\left\{\cos\left(\frac{(\Delta\omega_f)^2}{2\alpha}\right)\left[\pm C\left|\frac{\Delta\omega_i}{(\pi\alpha)^{1/2}}\right| \pm C\left|\frac{\Delta\omega_f}{(\pi\alpha)^{1/2}}\right|\right] + \sin\left(\frac{(\Delta\omega_f)^2}{2\alpha}\right)\left[\pm S\left|\frac{\Delta\omega_i}{(\pi\alpha)^{1/2}}\right| \pm S\left|\frac{\Delta\omega_f}{(\pi\alpha)^{1/2}}\right|\right]\right\}$$

Signal Scaling with Bandwidth

FT-Limited Pulse

$$\psi = a|a\rangle + b|b\rangle$$

$$|ab| = \sin\left(\frac{\mu_{ab}E\tau_c}{\hbar}\right) \approx \frac{\mu_{ab}E\tau_c}{\hbar}$$

$$\begin{aligned}
P = N\langle\mu\rangle &= N\mathrm{Tr}[\rho\mu] \\
&= N(ab\,\mu_{ab} + \mathrm{c.c.}) \\
&\approx N|\mu_{ab}|^2 E\tau_c/\hbar \\
&= \frac{|\mu_{ab}|^2 EN}{2\pi\hbar\Delta\nu_c}
\end{aligned}$$

Chirped Pulse

McGurk, J. C.; Schmalz, T. G.; Flygare, W. H. *J. Chem. Phys.* **60**, 4181, (1974).

Direct integration of Bloch Equations

$$0 = \frac{dP_r}{dt} + \Delta\omega P_i + \frac{P_r}{T_2}$$

$$0 = \frac{dP_i}{dt} - \Delta\omega P_r + |\mu_{ab}|^2 E\left(\frac{\Delta N}{\hbar}\right) + \frac{P_i}{T_2}$$

$$0 = \frac{d}{dt}\left(\frac{\hbar\Delta N}{4}\right) - EP_i + \frac{\hbar}{4}\frac{(\Delta N - \Delta N_0)}{T_1}$$

Assume   1. Population Transfer is Small
2. No Decay

$$0 = \alpha\frac{dP_r}{d\Delta\omega} + \Delta\omega P_i$$

$$0 = \alpha\frac{dP_i}{d\Delta\omega} - \Delta\omega P_r + |\mu_{ab}|^2 E\left(\frac{\Delta N_0}{\hbar}\right)$$

$$P_r(\Delta\omega_f) \propto \frac{|\mu_{ab}|^2 E}{\hbar}\Delta N_0\left(\frac{\pi\tau}{\Delta\nu}\right)^{1/2}\left\{\sin\left(\frac{(\Delta\omega_f)^2}{2\alpha}\right)\left[\pm C\left|\frac{\Delta\omega_i}{(\pi\alpha)^{1/2}}\right| \pm C\left|\frac{\Delta\omega_f}{(\pi\alpha)^{1/2}}\right|\right] - \cos\left(\frac{(\Delta\omega_f)^2}{2\alpha}\right)\left[\pm S\left|\frac{\Delta\omega_i}{(\pi\alpha)^{1/2}}\right| \pm S\left|\frac{\Delta\omega_f}{(\pi\alpha)^{1/2}}\right|\right]\right\}$$

$$P_i(\Delta\omega_f) \propto -\frac{|\mu_{ab}|^2 E}{\hbar}\Delta N_0\left(\frac{\pi\tau}{\Delta\nu}\right)^{1/2}\left\{\cos\left(\frac{(\Delta\omega_f)^2}{2\alpha}\right)\left[\pm C\left|\frac{\Delta\omega_i}{(\pi\alpha)^{1/2}}\right| \pm C\left|\frac{\Delta\omega_f}{(\pi\alpha)^{1/2}}\right|\right] + \sin\left(\frac{(\Delta\omega_f)^2}{2\alpha}\right)\left[\pm S\left|\frac{\Delta\omega_i}{(\pi\alpha)^{1/2}}\right| \pm S\left|\frac{\Delta\omega_f}{(\pi\alpha)^{1/2}}\right|\right]\right\}$$
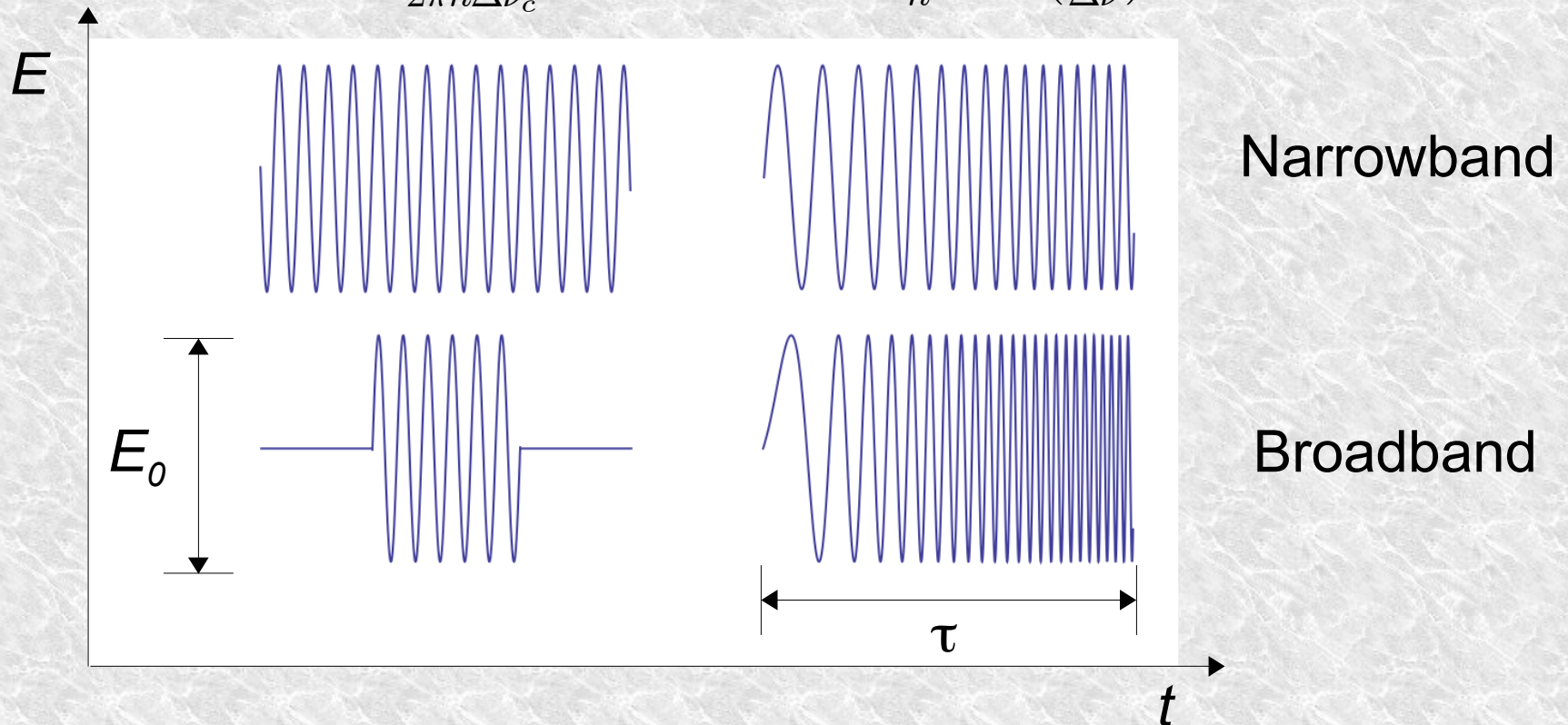
Signal Scaling with Bandwidth

FT-Limited Pulse

$$P \approx \frac{|\mu_{ab}|^2 E_0 \Delta N_0}{2\pi\hbar\Delta\nu_c}$$

Chirped Pulse

$$P \propto \frac{|\mu_{ab}|^2 E_0 \Delta N_0}{\hbar} \left(\frac{\pi\tau}{\Delta\nu}\right)^{1/2}$$

E

E_0
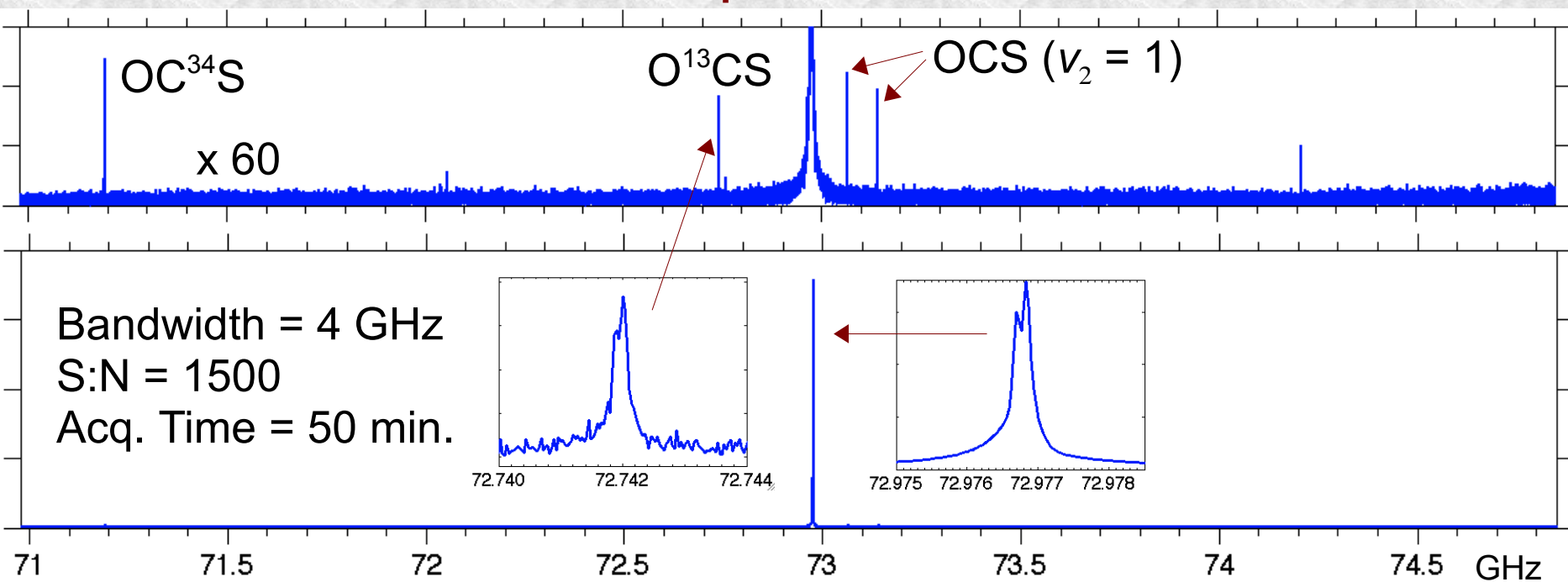
Narrowband

Broadband

τ

t
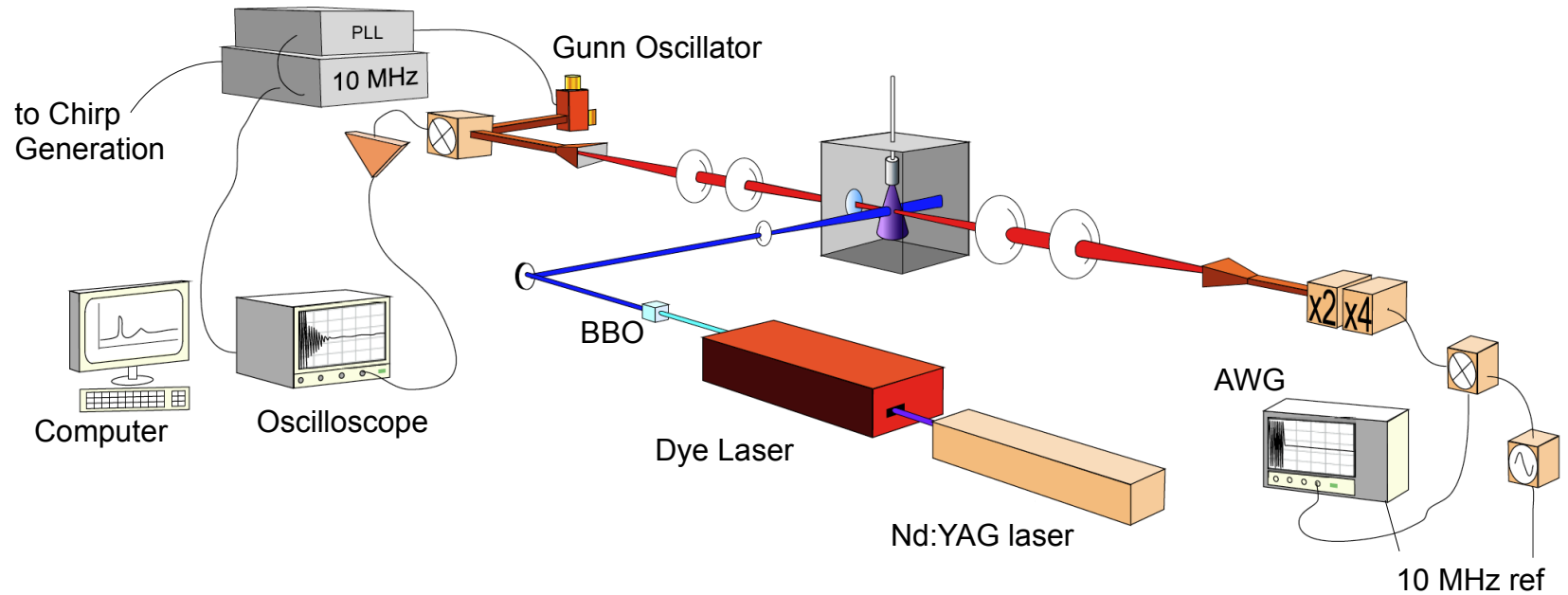
Balle-Flygare Cavity FT

The Yamamoto Balle-Flygare spectrometer can take spectra of similar S:N with 2-3 averages per cavity position. Total acquisition time ~ 4 hours.

Yamamoto, S.; Habara, H.; Kim, E.; Nagasaka, H. *J. Chem. Phys.* **115**, 6007, (2001).

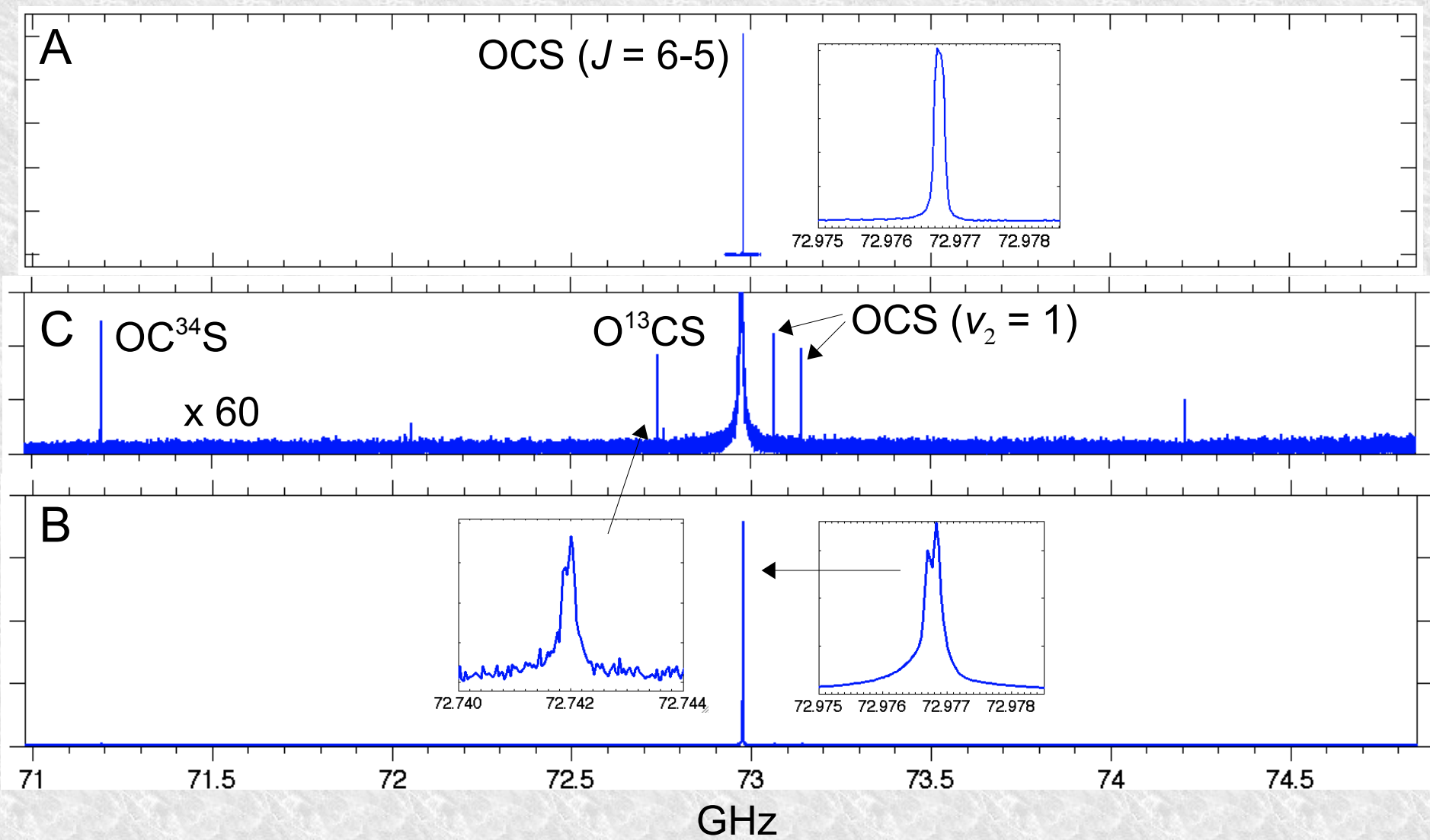## Chirped Pulse

Our CPmmW Spectrometer

Power Requirements
Single-Frequency Pulse

Assume 1 D transition dipole moment, 1 cm^2 focus, and 1 μs interaction time ($\Delta\omega$ = 160 kHz).
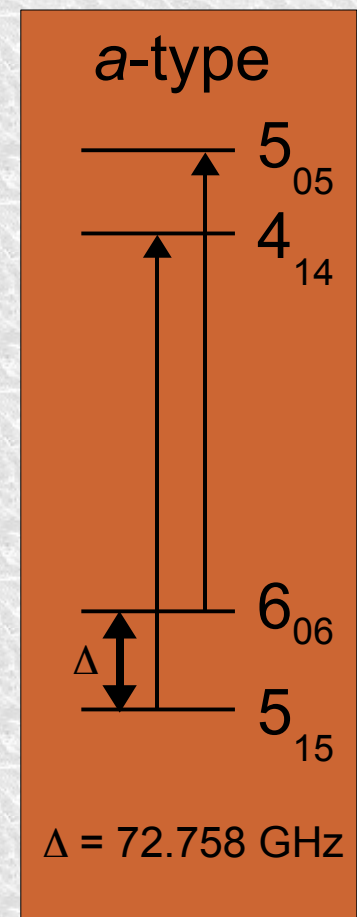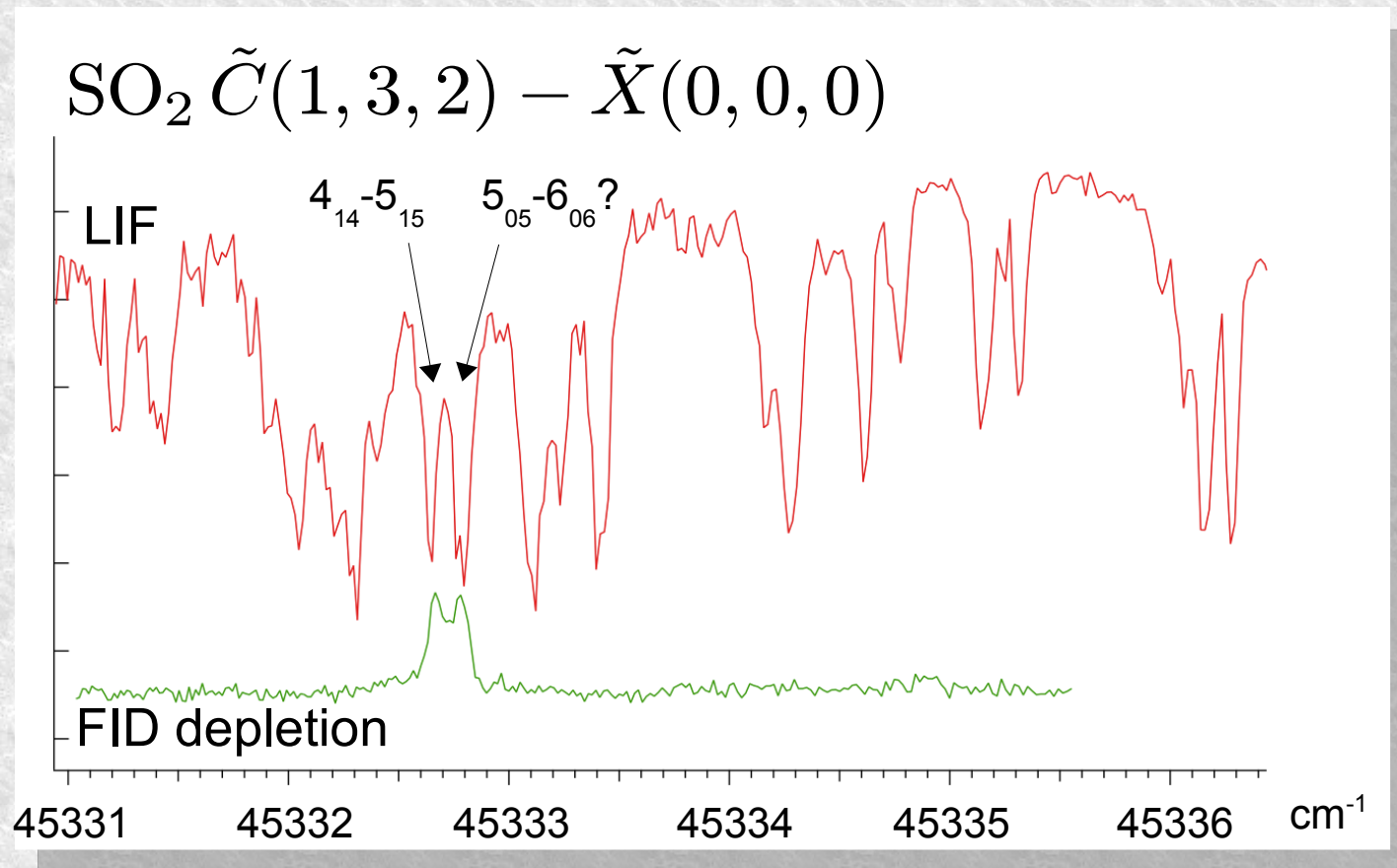
Optimum excitation occurs when $\mu_{ab}Et/\hbar = \pi/2$, or E = 50 V/m. This corresponds to a power of 0.31 mW or -4.8 dBm.

$$I = \frac{\epsilon_0 c E^2}{2} \qquad P = IA$$

How much power is required for optimal excitation with a broadband pulse?

A — OCS (J = 6-5)

C — OC^{34}S   x 60   O^{13}CS   OCS (v_2 = 1)

B

Laser-CPmmW Double Resonance

$SO_2 \, \tilde{C}(1,3,2) - \tilde{X}(0,0,0)$

LIF

4_{14}-5_{15} 5_{05}-6_{06}?

FID depletion

45331   45332   45333   45334   45335   45336 cm^{-1}

a-type
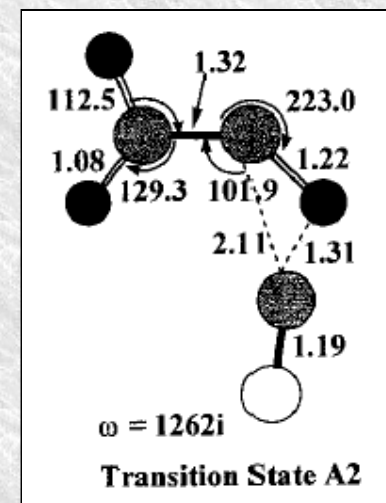
5_{05}

4_{14}

6_{06}

Δ

5_{15}

Δ = 72.758 GHz

Assignments: K. Yamanouchi, *et al*., *J. Mol. Struct.* **352/353**, 541, (1995)

Acrylonitrile Photolysis

$$C_2H_3CN \xrightarrow{193\ nm} Products$$

$$C_2H_3CN \rightarrow C_2H_2 + HCN\ (HNC) \quad (1)$$
$$\rightarrow C_2HCN + H_2 \quad (2)$$
$$\rightarrow C_2H_3 + CN \quad (3)$$
$$\rightarrow C_2H_2CN + H \quad (4)$$
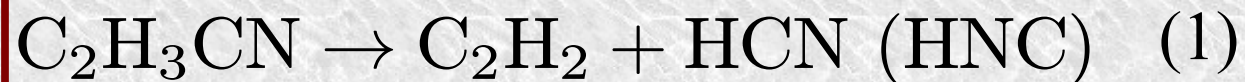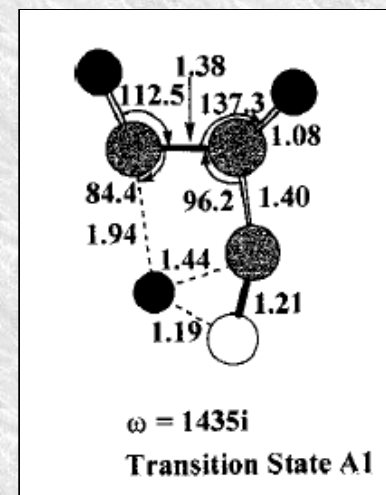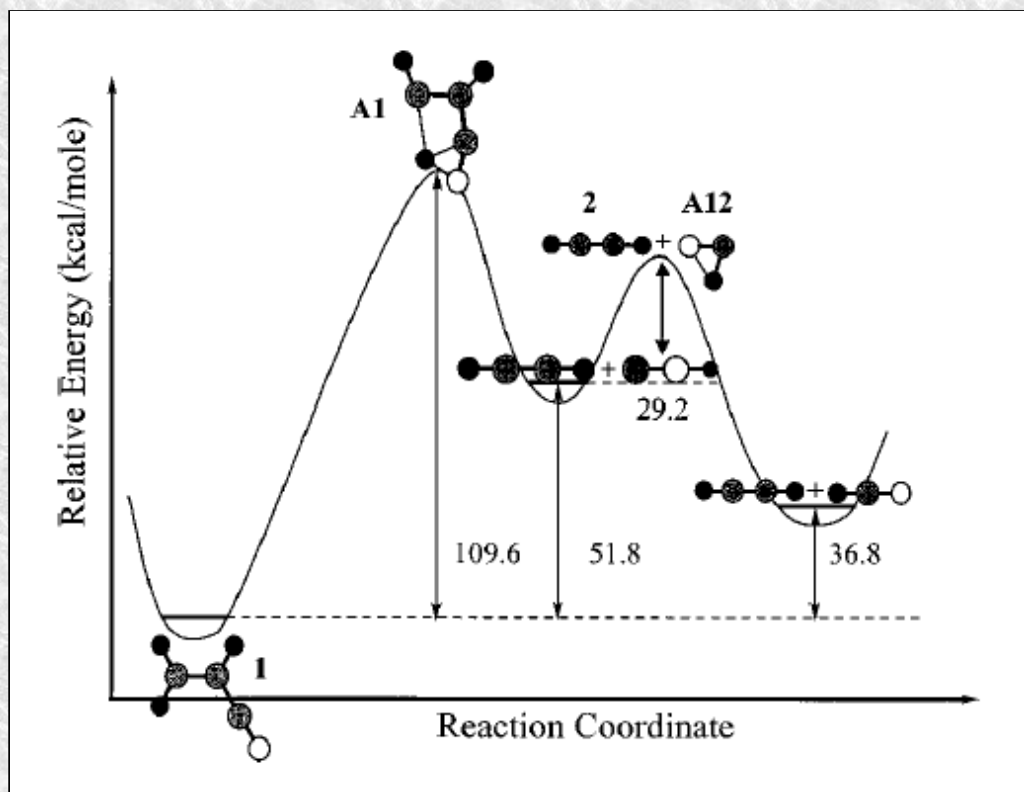
Acrylonitrile Photolysis
Three-Center mechanism yields HCN
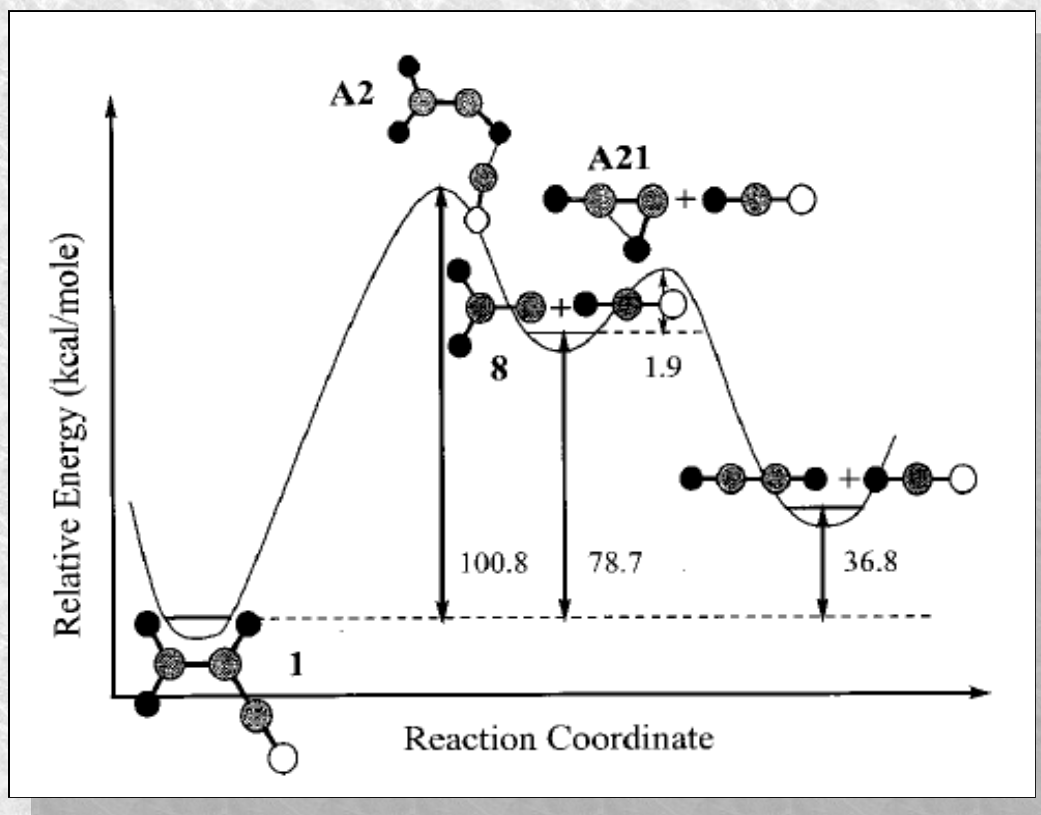
A. Derecskei-Kovacs and S.W. North. *J. Chem. Phys.* **110**, 2862 (1999).

Acrylonitrile Photolysis
Four-Center mechanism yields HNC (HCN)

A. Derecskei-Kovacs and S.W. North. *J. Chem. Phys.* **110**, 2862 (1999).

Controversy Over the Mechanism

Three Center

- Calculations[1]
    - *ab initio* calculations: Transition state is ~10 kcal/mol lower.
    - RRKM rate calculations: Three-center mechanism is 100 times faster.

- Experiment
    - Acrylonitrile-1-*d* yields DCN.[2]
    - Translational release consistent with three-center mechanism.[3]

Four Center

- "HCN" ionization onset anomalously low (2.6 eV).[3]

- TR-FTIR[4] and mmW[5] spectroscopy reveal HNC.

1. A. Derecskei-Kovacs and S.W. North. *J. Chem. Phys.* **110**, 2862 (1999).
2. Fahr, A.; Laufer, A.H. *J. Phys. Chem.* **96**, 4217, (1992).
3. Blank, D.A.; Suits, A.G.; Lee, Y.T.; North, S.W.; Hall, G.E. *J. Chem. Phys.* **108**, 5784, (1998).
4. Dai, H.-L. Unpublished results (2005).
5. Bechtel, H.A.; Steeves, A.H.; Field, R.W. *61st OSU ISMS*, conference proceedings, (2006).

Going Further

Photolysis, SEP and the HNC S_1 surface

- The mechanism for 193 nm photolysis of acrylonitrile is poorly understood

- If HNC states of $v_{CN} > 2$ are found, this may grant access to HNC S_1 states.

- May serve as a new vantage point for finding delocalized S_0 states.

Zhou, S.; Xie, D.; Xu, D.; Guo, H, Field, R.W.; *Chem. Phys. Lett.* **455**, 145 (2008).