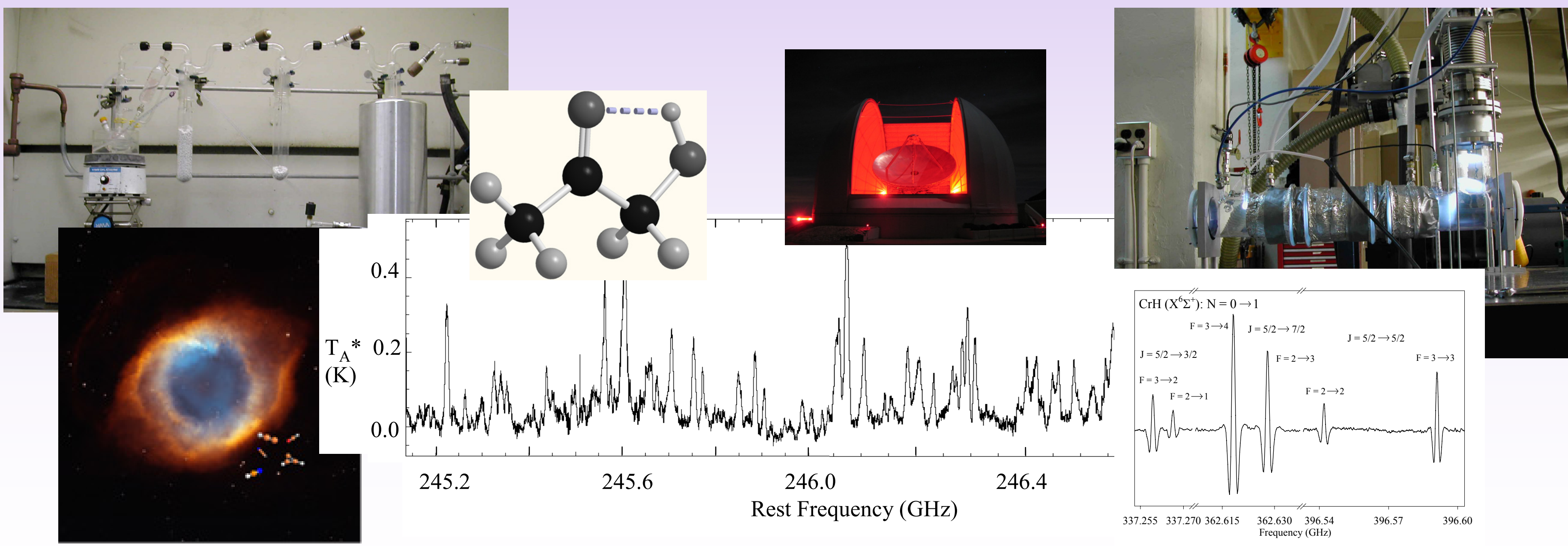
Laboratory Spectroscopic Techniques

Lucy M. Ziurys, Aldo J. Apponi,
DeWayne T. Halfen, Michael A. Flory, Chandra Savage, and
Matthew A. Brewster
Depts. of Chemistry and Astronomy
University of Arizona



Arizona Radio Observatory

Spectroscopy Applicable to Submm Astronomy

- **Type of Molecules** Involved

⇒ Many Interstellar Molecules ***common terrestrial species***

- CH_3OH, H_2O, H_2CO, CH_3OCH_3, etc.

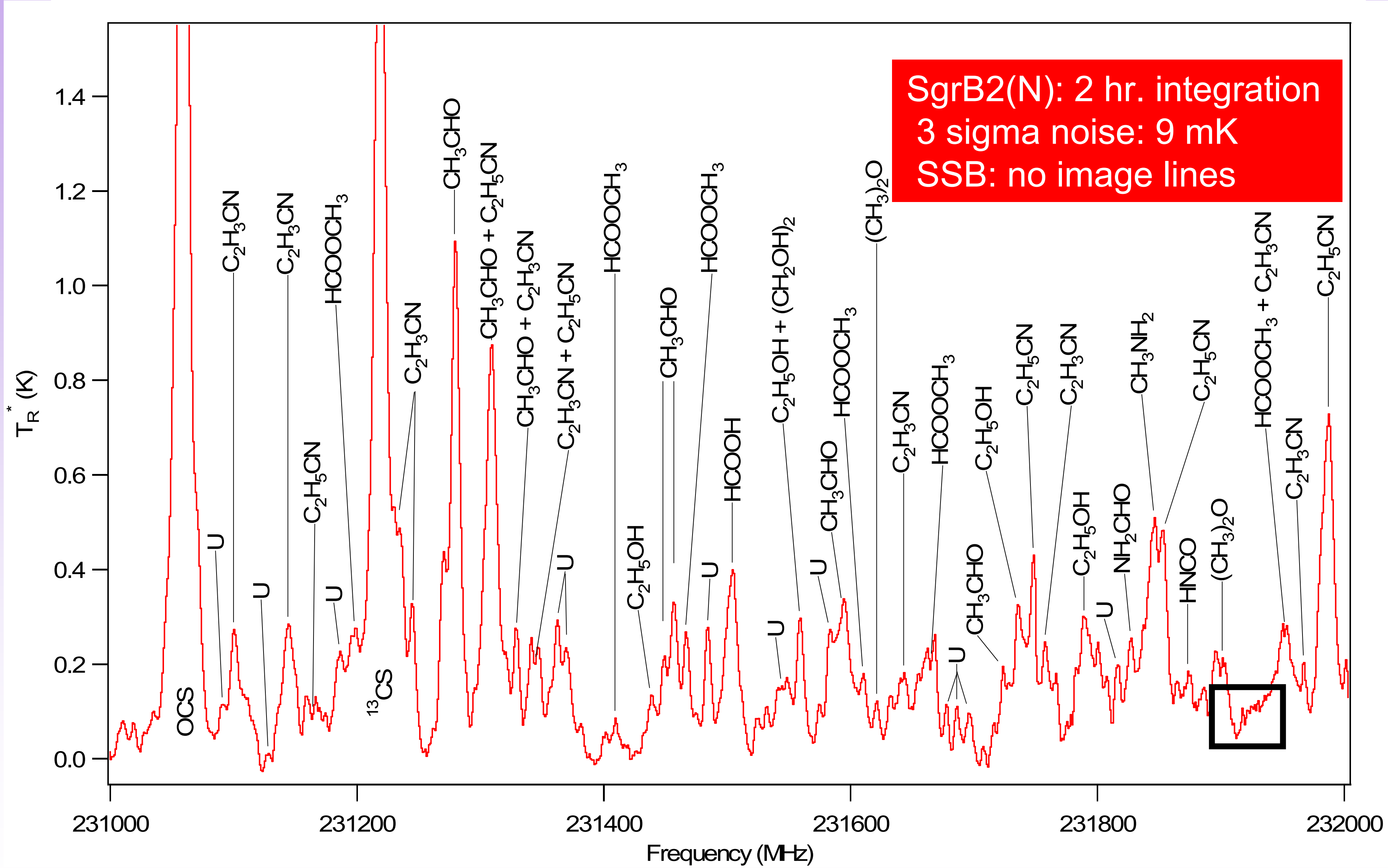
⇒ More ***than 50%*** of all interstellar species are ***"non-terrestrial"***

- Free radicals, molecular ions, metastable isomers (HCO^+, CH, C_8H, HNC)

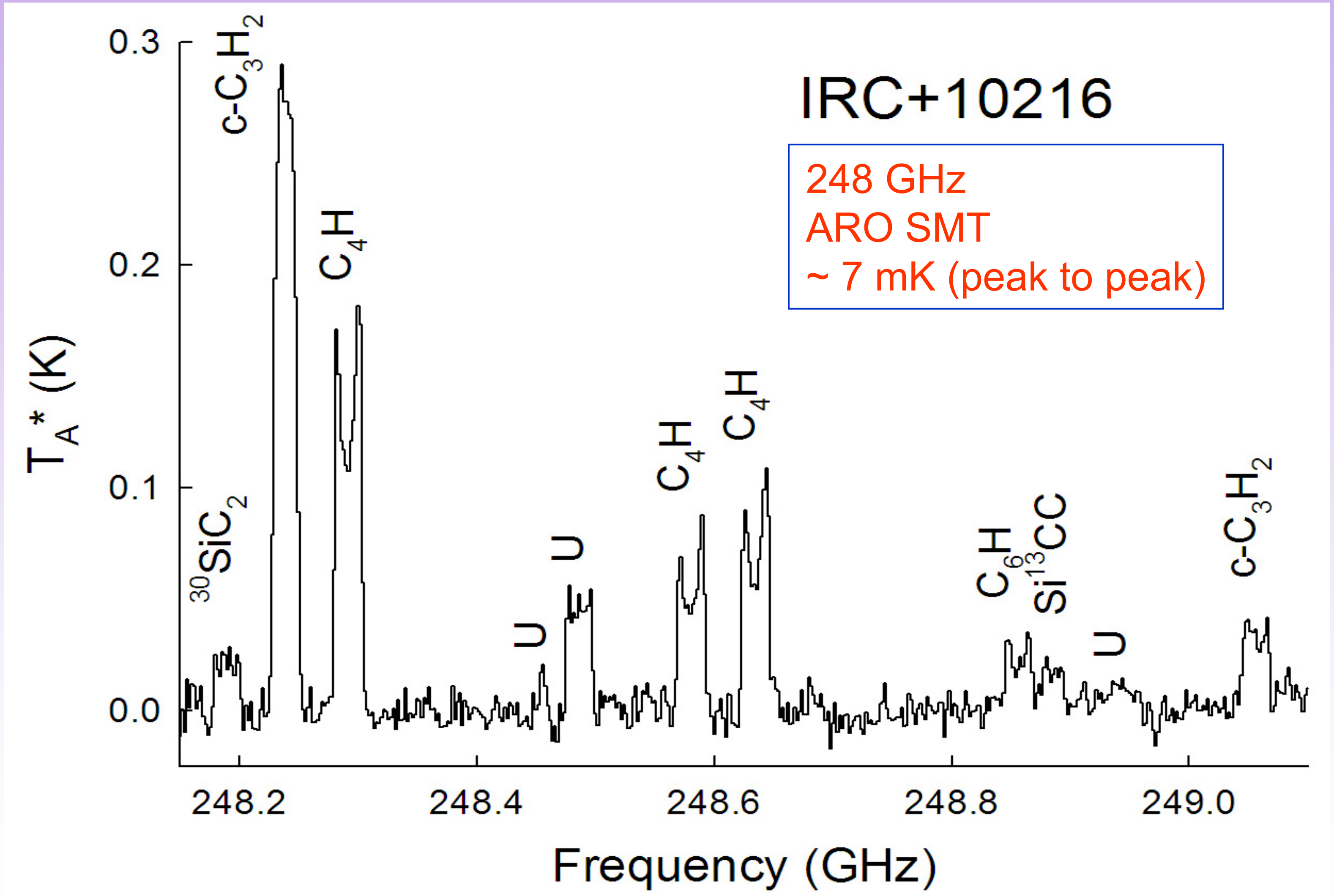
- Nature of **Interstellar Spectra** (Gas-Phase)
  - Interstellar gas is basically ***cold*** (T ~ 10 -200 K)
  - Populate ***pure rotational levels***, including vibrational satellite lines
  - Populated by collisions: ***Linewidths narrow***
  - Heterodyne techniques enable ***high resolution measurements***

⇒ high sensitivity spectra: ***rich in molecular lines***

NEED HIGH RESOLUTION LAB SPECTROSCOPY
WITH CLEVER SYNTHETIC METHODS


SgrB2(N): 2 hr. integration
3 sigma noise: 9 mK
SSB: no image lines
T_R^* (K)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
231000
231200
231400
231600
231800
232000
Frequency (MHz)
OCS
U
C_2H_3CN
U
C_2H_3CN
C_2H_5CN
U
$HCOOCH_3$
^{13}CS
C_2H_3CN
CH_3CHO
$CH_3CHO + C_2H_5CN$
$CH_3CHO + C_2H_3CN$
$C_2H_3CN + C_2H_5CN$
U
$HCOOCH_3$
C_2H_5OH
CH_3CHO
$HCOOCH_3$
U
HCOOH
U
$C_2H_5OH + (CH_2OH)_2$
U
CH_3CHO
$HCOOCH_3$
$(CH_3)_2O$
C_2H_3CN
$HCOOCH_3$
U
CH_3CHO
C_2H_5OH
C_2H_5CN
C_2H_3CN
C_2H_5OH
U
NH_2CHO
CH_3NH_2
C_2H_5CN
HNCO
$(CH_3)_2O$
$HCOOCH_3 + C_2H_3CN$
C_2H_3CN
C_2H_5CN

- But not all interstellar spectra are at the confusion limit…



Many discrete U-lines exist !

Techniques in High Resolution Spectroscopy

- Interstellar studies require ***accurate gas-phase*** lab spectra
  - Experimental Precision of **1 part in 10^7 -10^8**

⇒ Limits techniques to ***pure rotational spectroscopy***

  - Some optical/IR methods claim high resolution

⇒ Nothing is better than DIRECT MEASUREMENT of given transition

  - Lab spectra **properly assigned** and **well understood**
  - **Molecular Physics** involved, not a **“data-base creation”**

- Most common methods in Rotational Spectroscopy

1) Millimeter/Sub-millimeter Direct Absorption Methods

2) Pulsed Fourier Transform Microwave (FTMW) Technique

3) Velocity Modulation Spectroscopy

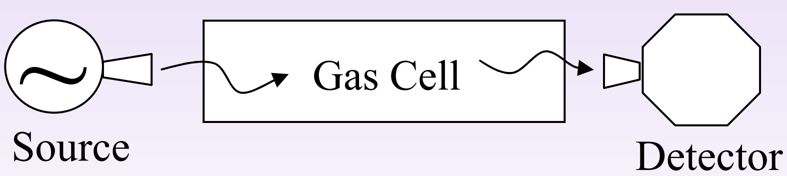
4) Far-IR Methods (LMR, TuFirs, Laser-Sideband Systems)

Millimeter/Sub-mm Direct Absorption Spectroscopy

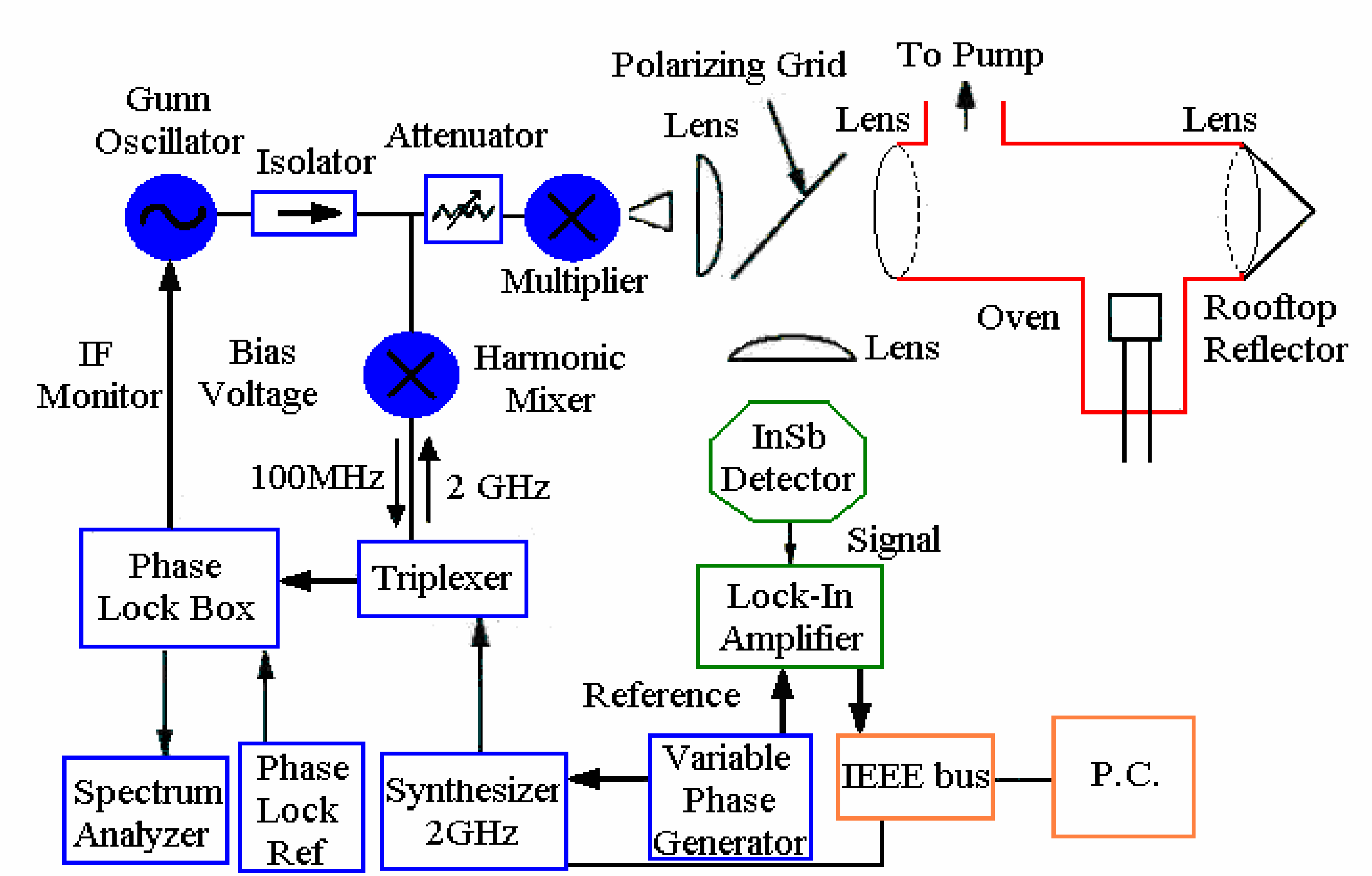
- In principle, very simple
  - **Radiation source** (Gunn diode, YIG or synthesizer/power amplifier with Schottky diode multipliers; BWO's)
  - "**Free-Space" gas cell** to contain molecules
  - He-cooled InSb **Bolometer Detector**

⇒ radiation source scanned in ν, sent through cell

⇒ absorption by molecules monitored by detector



- More complicated
  - **Sub-mm/THz sources** can be problematic to obtain and use
  - **Not as sensitive** as photon-counting techniques (~ 10^8 -10^{10} molecules)
  - **Baselines horrendous** (unless very careful with optics)



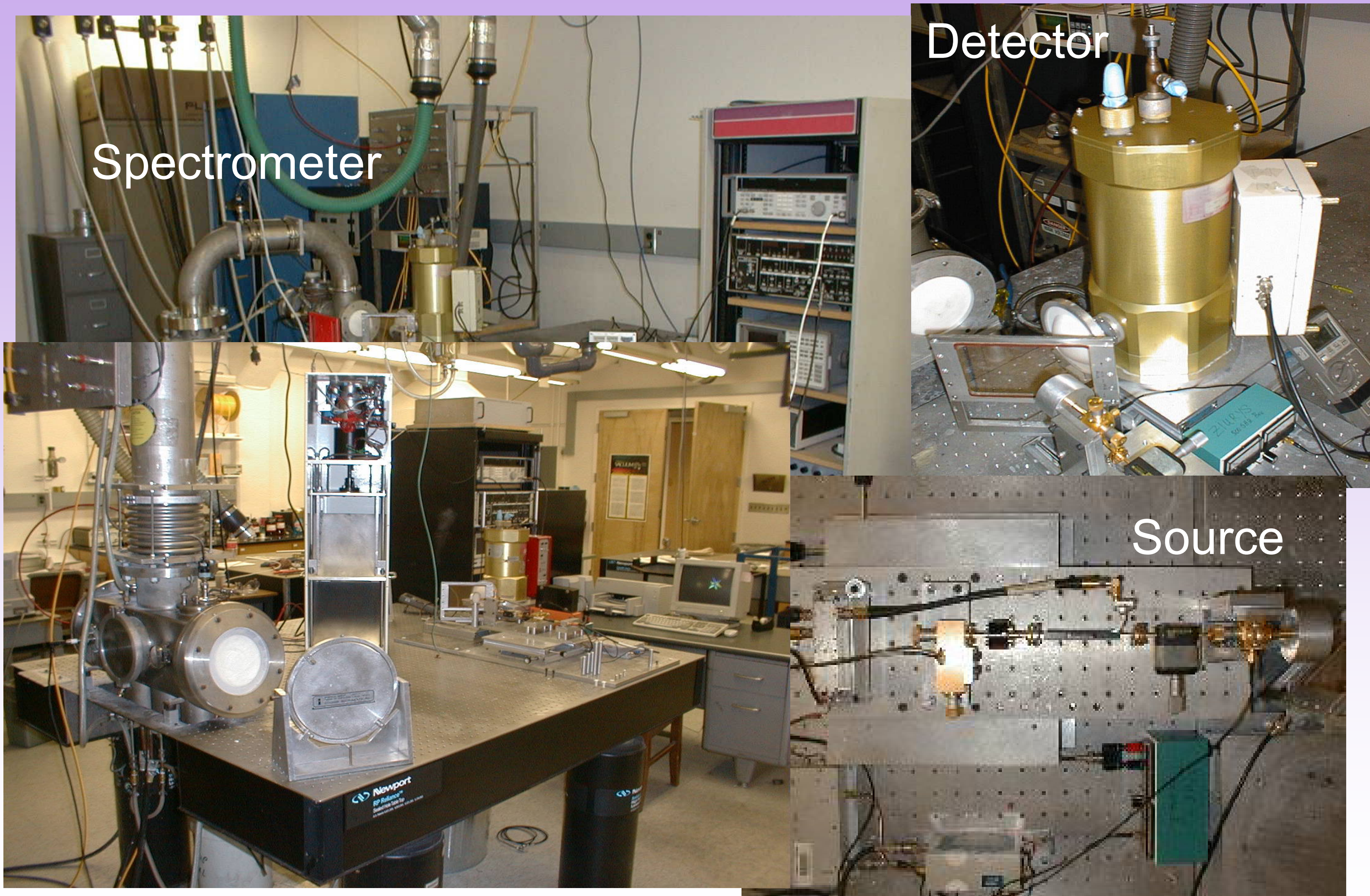
- Use complex electronics
- For reactive species: need Roots-blowers pump
- Typical pressures P ~ 50 – 100 mtorr
- Linewidths typically ~ 300 kHz – 1.5 MHz
- At 100 MHz BW per scan, search many GHZ

Block-Diagram of One of Arizona Systems

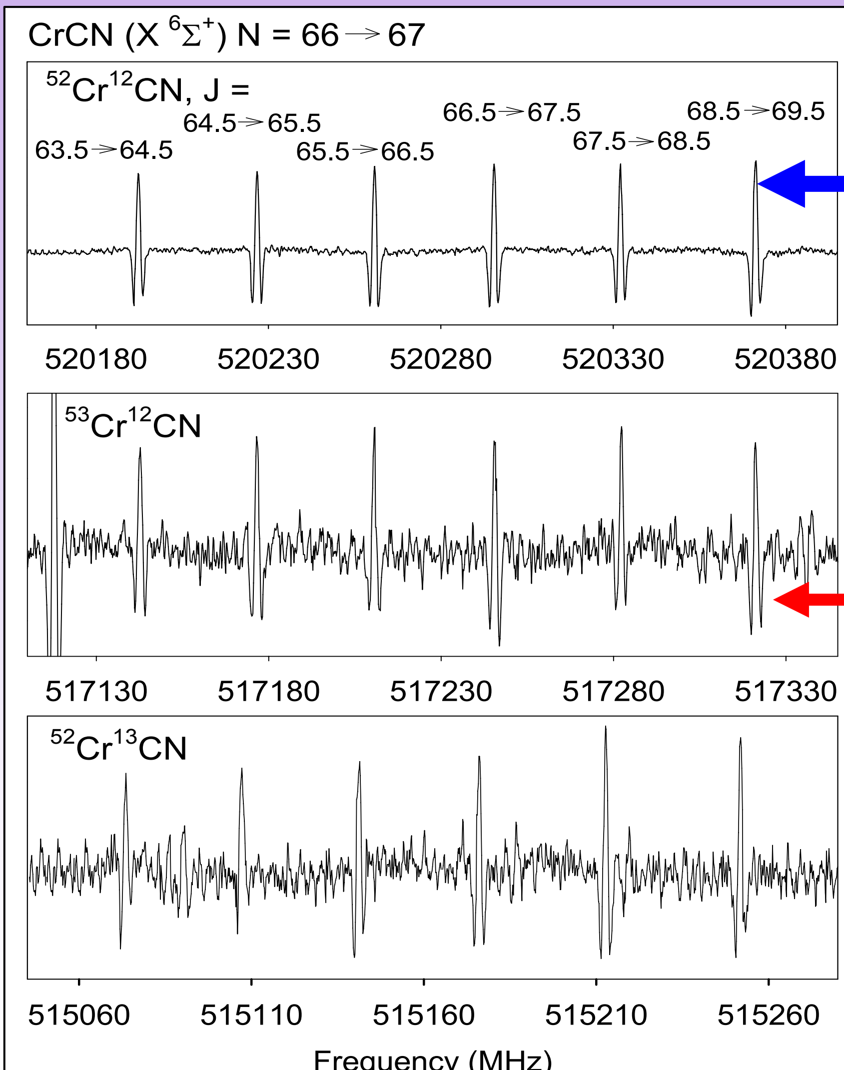
ADVANTAGES: Precision ± 50 – 100 kHz

⇒ 1 Part in 10^7 - 10^8

⇒ Direct measurements

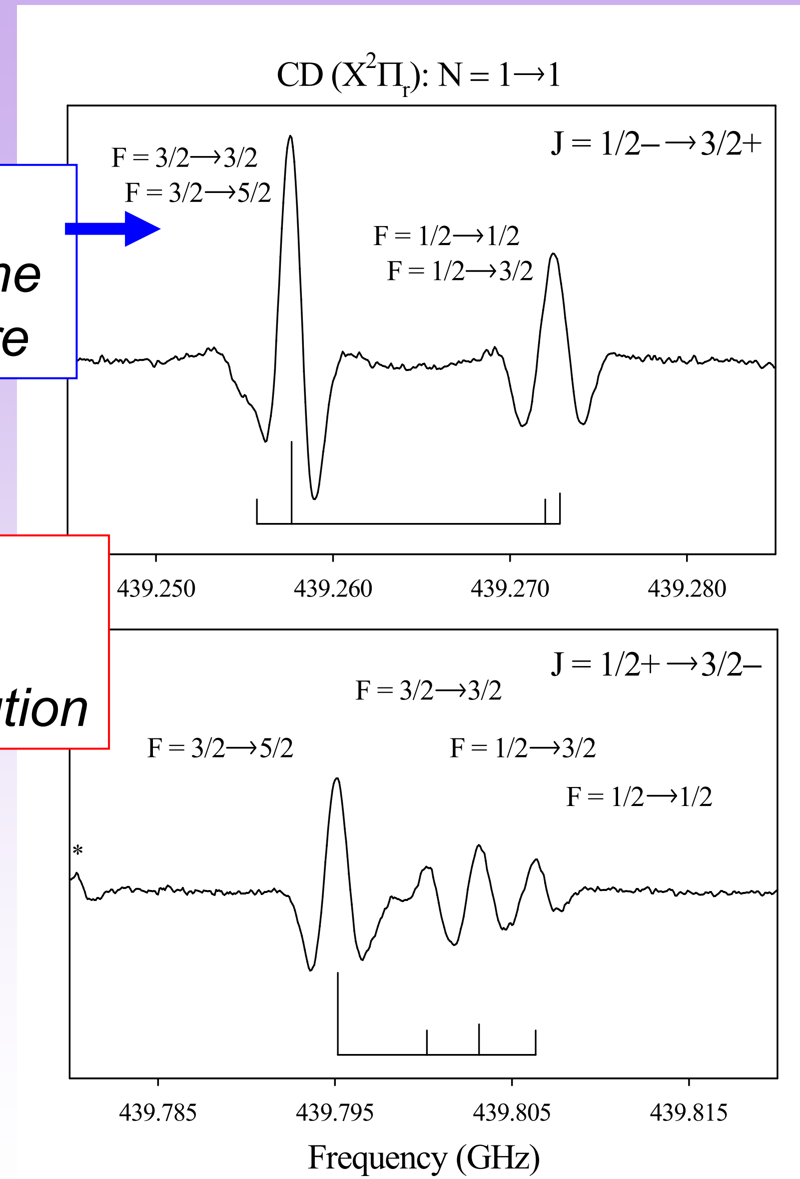

Spectrometer
Detector
Source

High Spectral Quality



Fine/ Hyperfine Structure

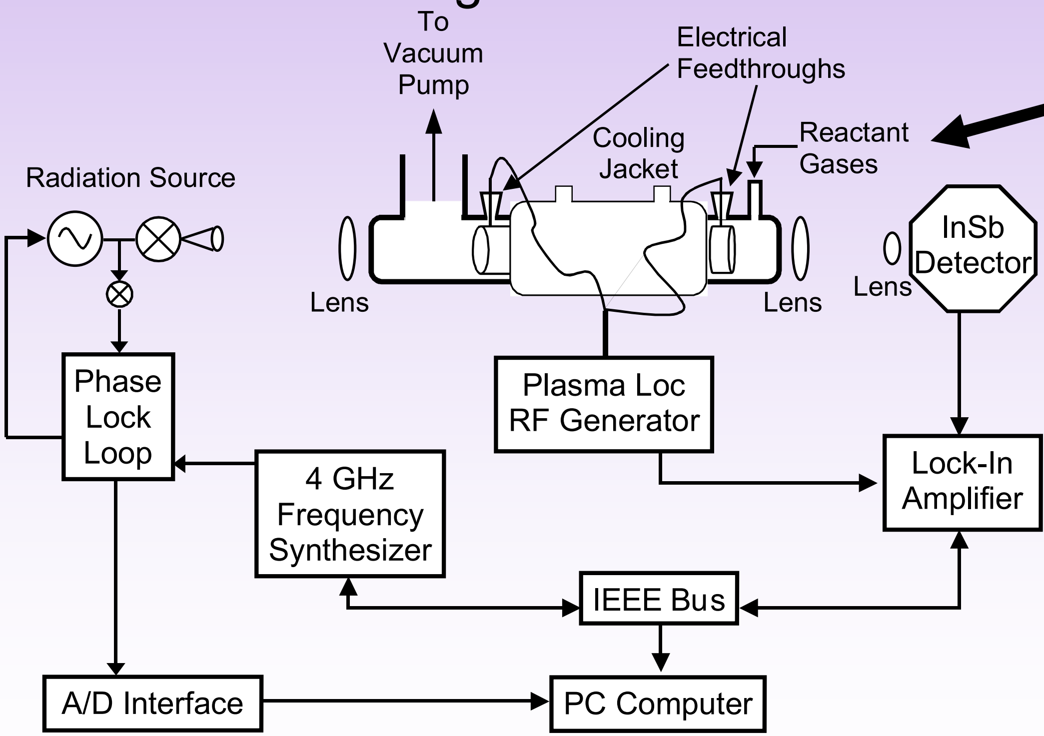
Multiple Isotopic Substitution

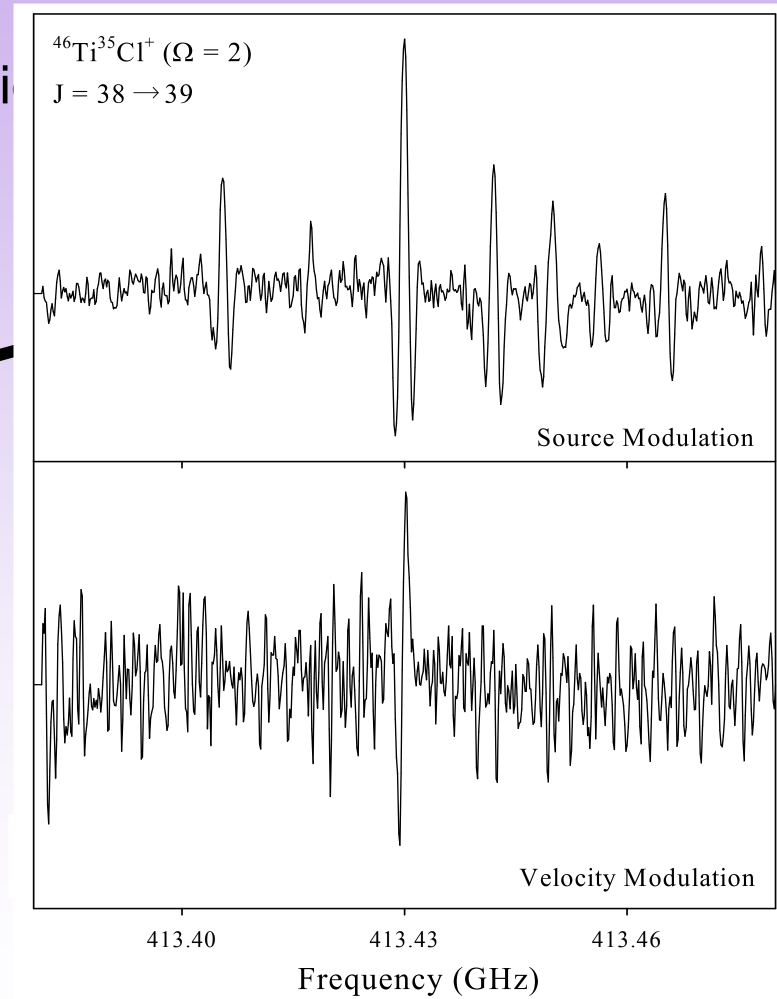


Arizona Radio Observatory

Millimeter/Sub-mm Velocity Modulation Spectroscopy

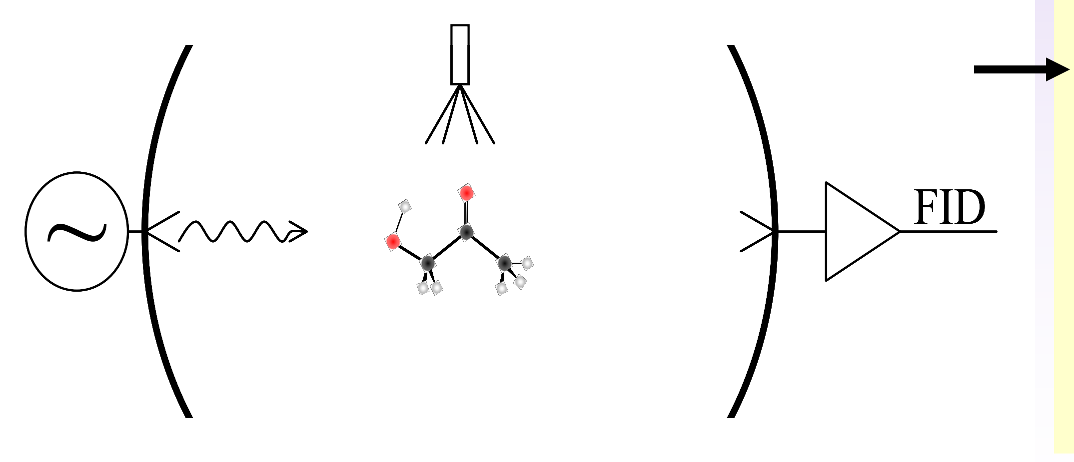
- Variation of Direct Absorption Methods
- Technique developed in the IR for ro-vibrati
- "Velocity modulate" ions in AC discharge
- Detect at discharge modulation rate

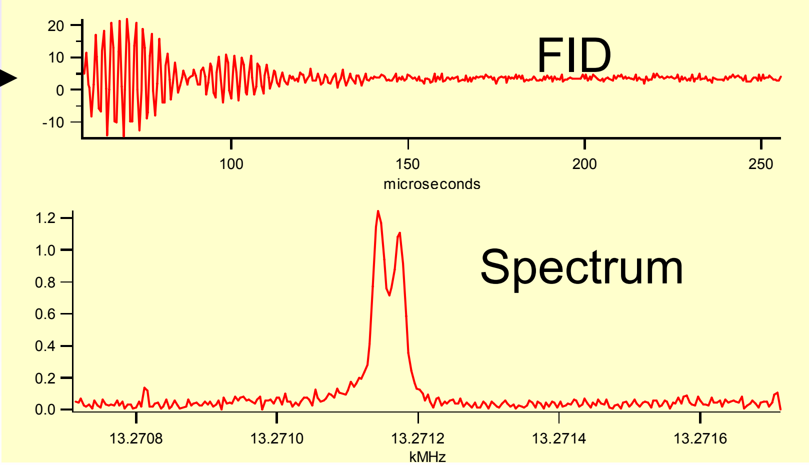


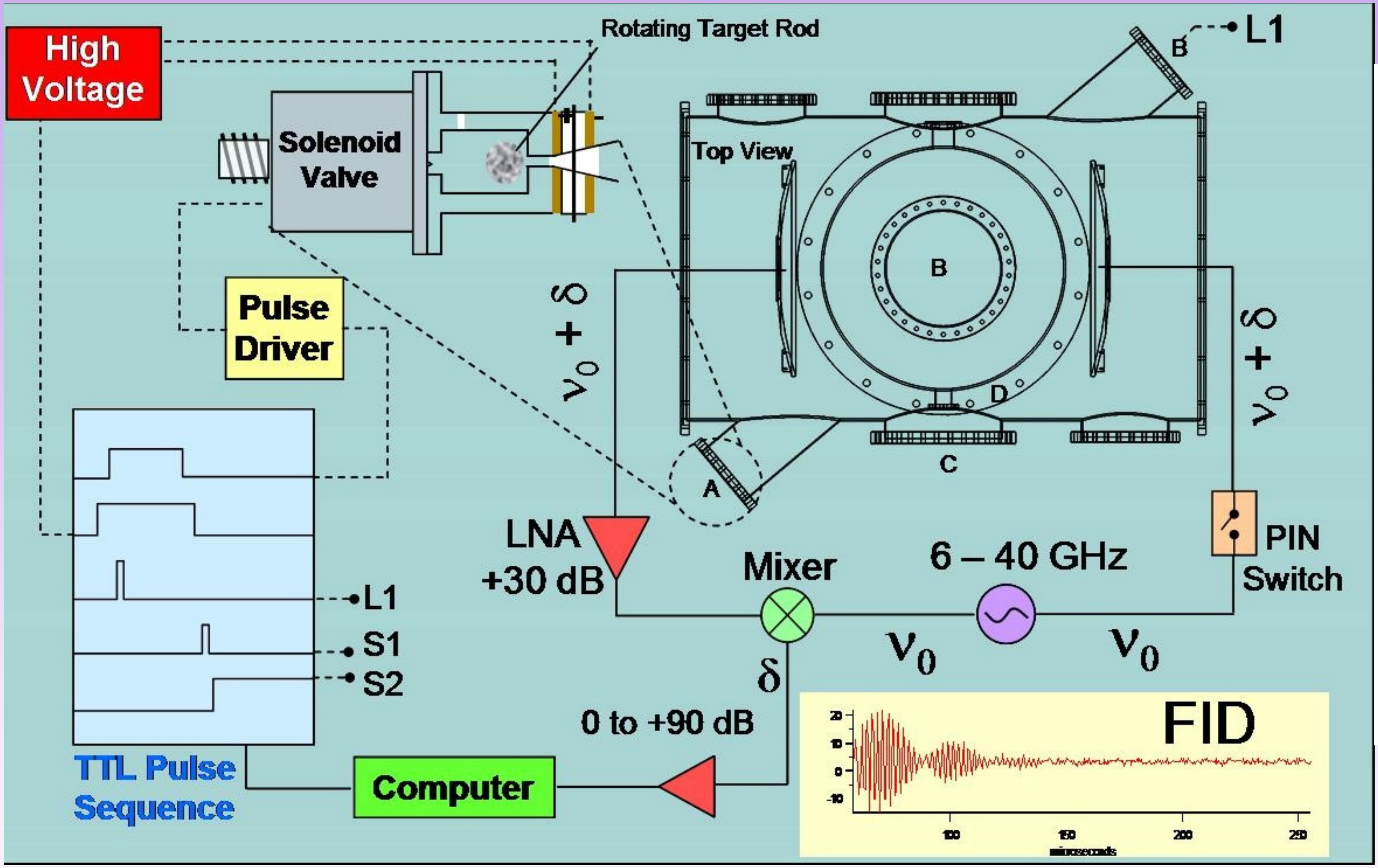


Pulsed Fourier-Transform Microwave Spectroscopy

- Not in sub-mm/far IR **(MICROWAVE ~ 3 – 52 GHz)**
- Useful: ***complements sub-mm studies***
- Basic method
  - Fabry-Perot cavity consisting of two mirrors
  - Molecules "pulsed" into cavity with supersonic nozzle
  - Excite with pulse of microwave radiation (10- 20 Hz rep. rate)
  - Monitor free induction decay (FID) with time
  - Fourier Transform of FID ⇒ spectrum

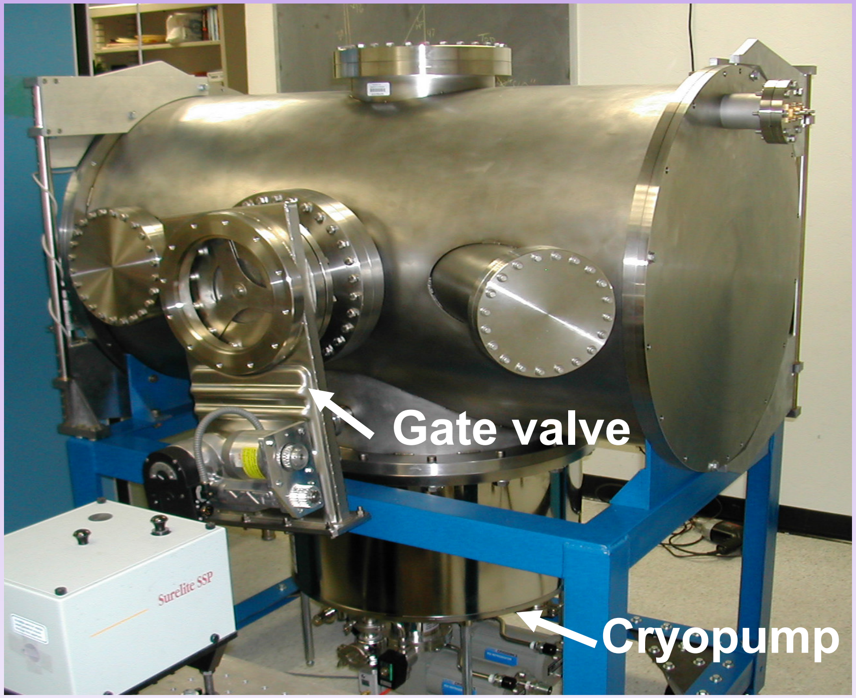






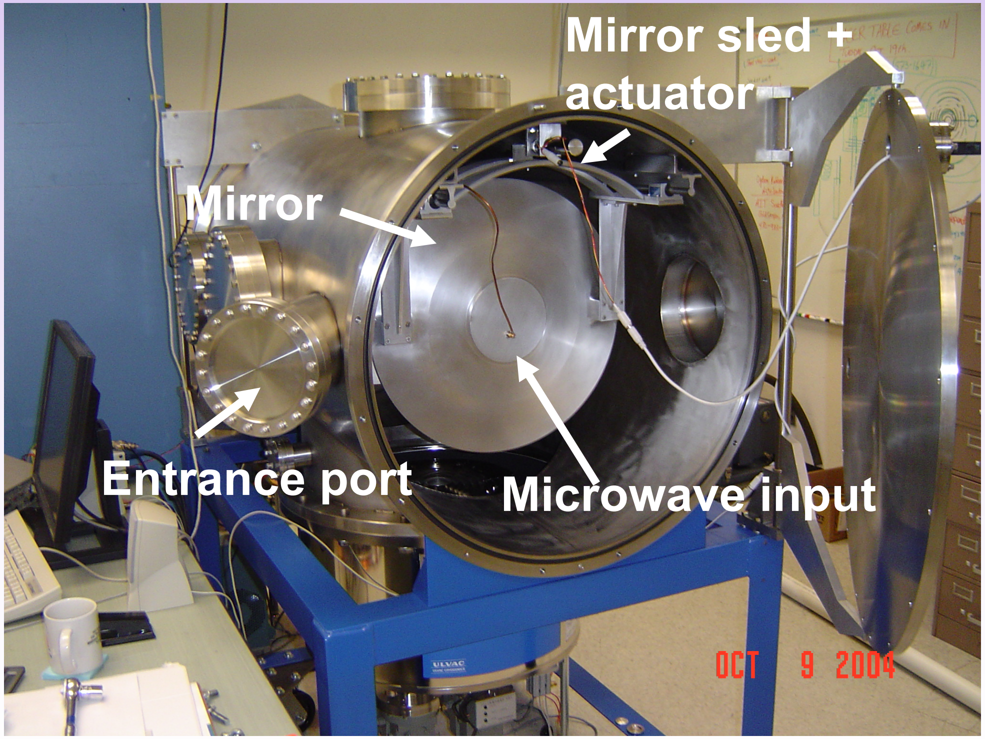
- Complication of nozzle source
- Complex timing of pulses
- Limited BW; harder to search
- Access only low energy transitions

- Higher sensitivity than direct absorption
- Narrow linewidths: resolution 5 – 10 kHz
- With discharge nozzle, new chemical regime



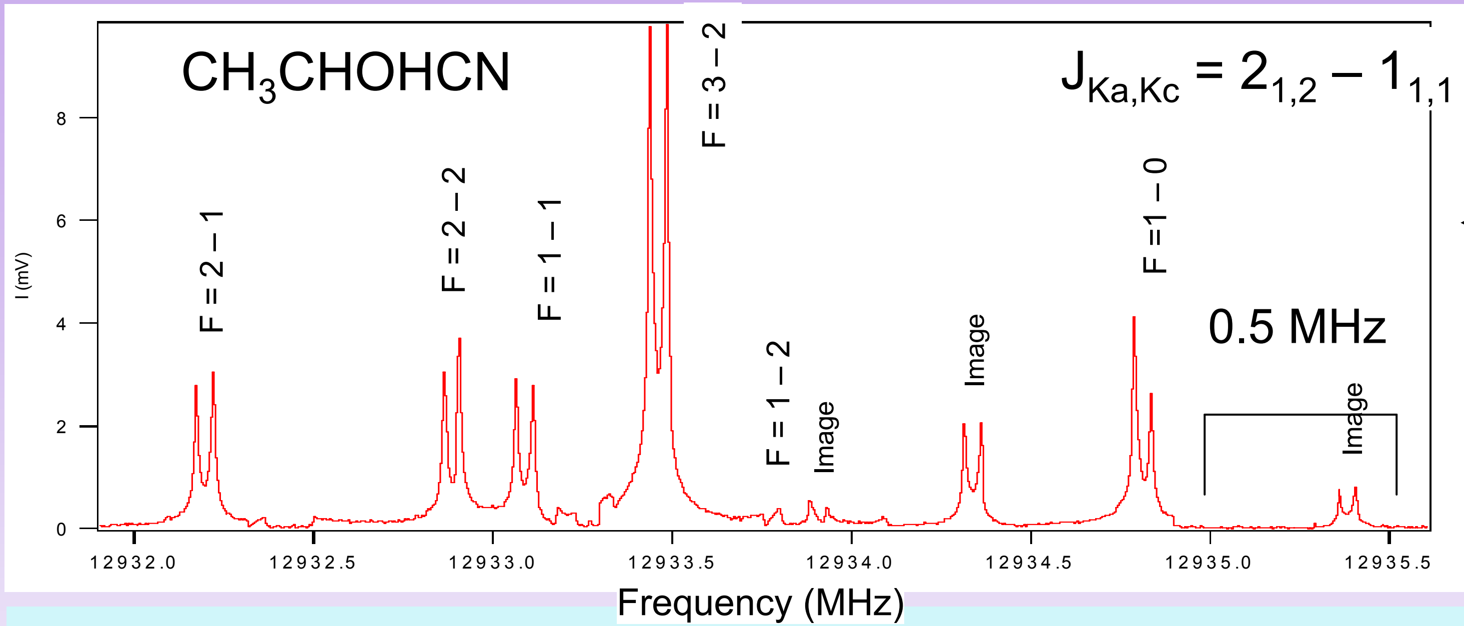
Arizona FTMW

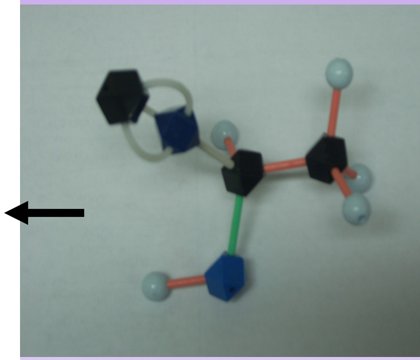
- Uses cryopump, not diffusion pump
- Supersonic beam at 40 deg.vs. perpendicular or through mirrors
- Mirrors encased in mu-metal shield (Zeeman effect from Earth's field)

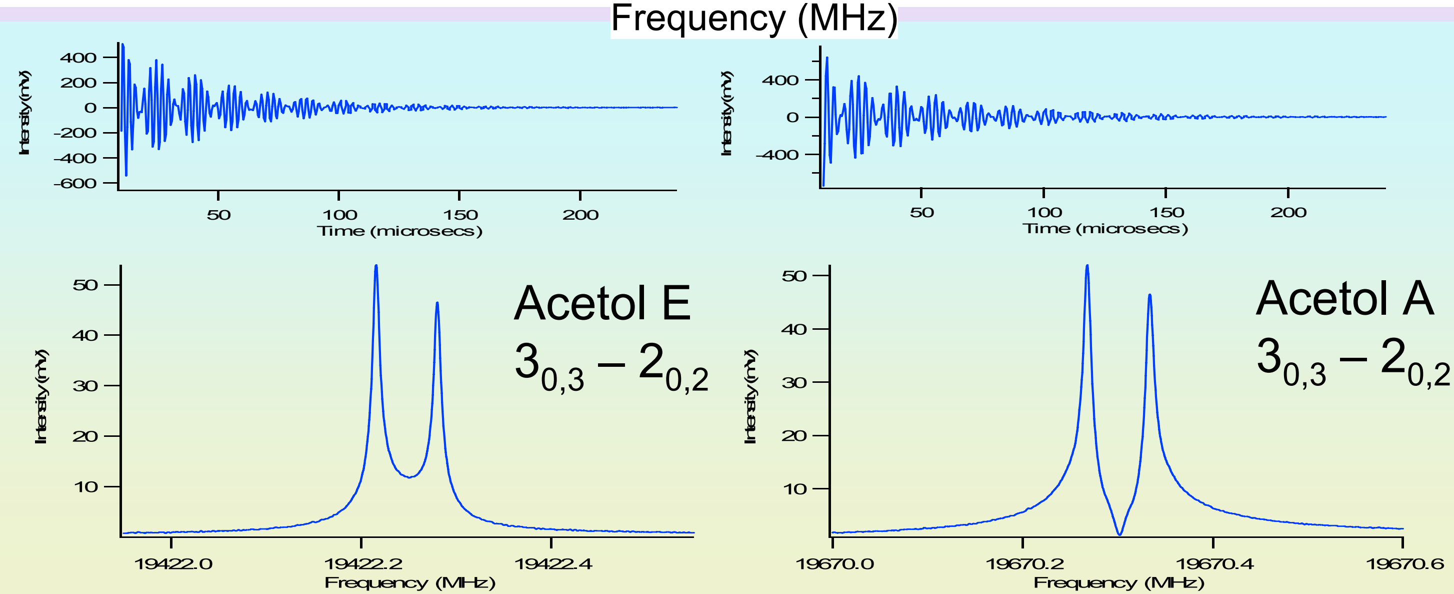


Future upgrades

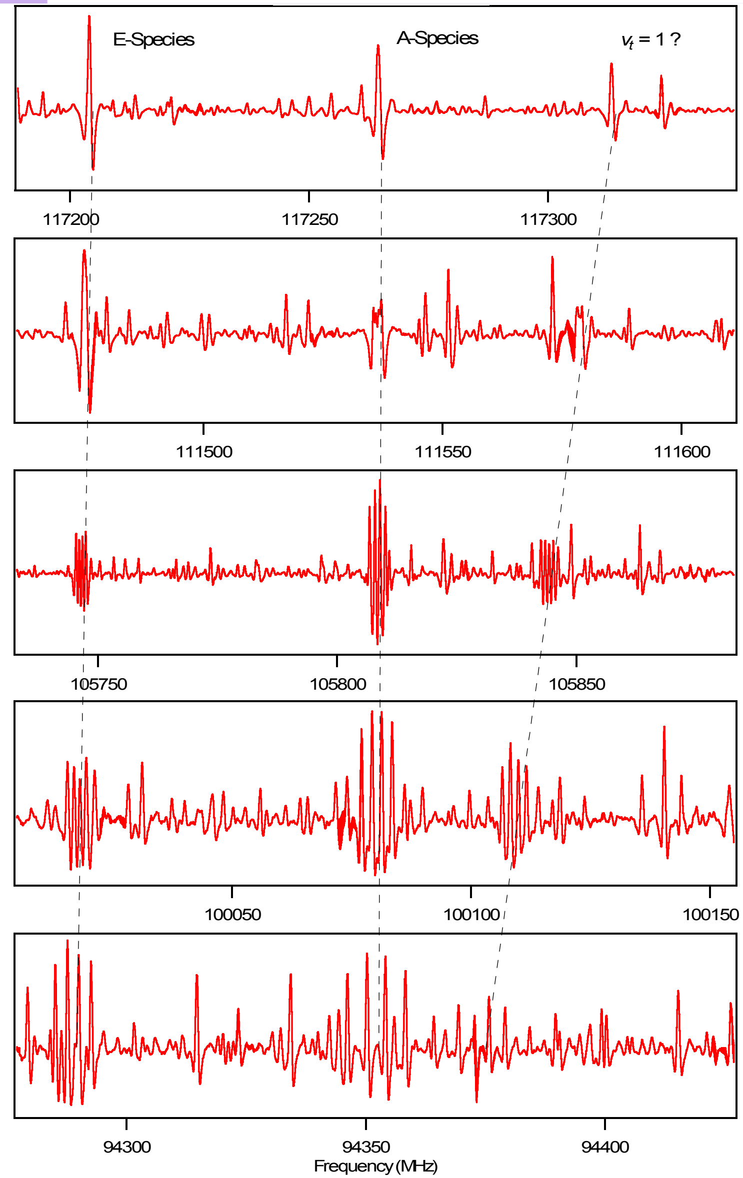
- Push frequency coverage up to 80 GHz with waveguide coupling
- Cryogenically cool optics and detection electronics to ~ 20 K



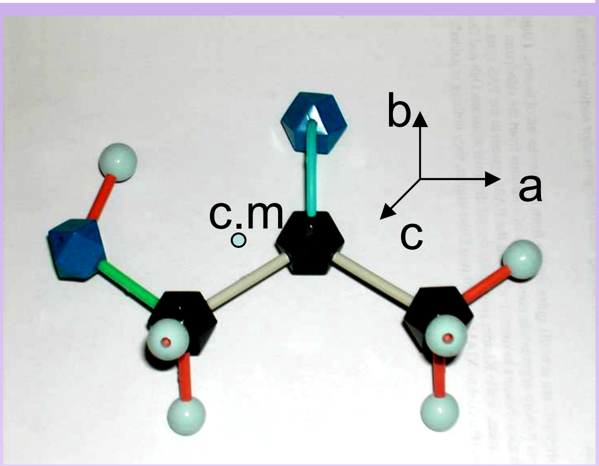




- Measure quadrupole/ magnetic hf structure
- Key to unraveling mm/sub-mm spectra



Acetol
CH_3COCH_2OH



- Internal rotor problem: methyl group
- A and E states
- E state of $v_t = 0$ mixes with E state of $v_t=1$
  - K no longer a good quantum number
- Complicated Analysis with Rho-axis method

⇒ FTMW data ***crucial*** in locking-in E state analysis

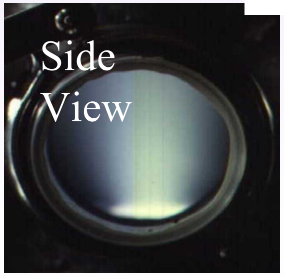
⇒ Past work E State mis-assigned

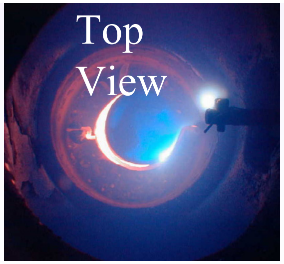
Molecule Production Techniques

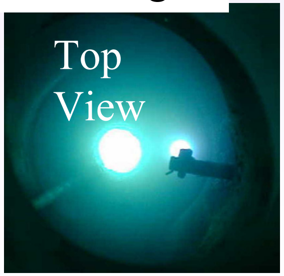
- Some molecules of interest come in bottles, gas cylinders
- ***Unstable Species*** pose many more problems
  - live for fractions of seconds
  - create in non-equilibrium conditions with DC, AC, microwave discharges
  - metal-containing species: Broida-type ovens or laser ablation
  - FTMW: discharge in nozzle
  - Dangerous chemicals (HCN, HCCCCH, SiH_4, etc)
- Creation of transient species a ***BLACK ART***

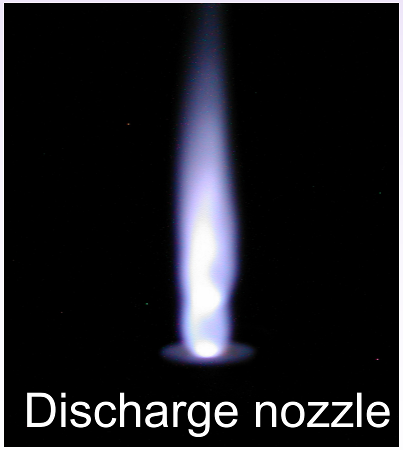
Better be a competent chemist !

Radicals in DC discharge









Identification of Laboratory Molecules

- Unstable species
  - Often **NO previous data** (low resolution), no theoretical calculations
  - An Intelligent Guess and Search
  - Searches may involve ***20 -100 GHz continuously*** in frequency space

  ⇒ Labor and material intensive, with no guarantees
  - Metals particularly problematic because **chemistry unpredictable**
- Stable Molecules have other difficulties
  - HIGH Spectral density of larger species at room temperature
  - Almost continuous features
  - Easy to misassign **weaker transitions** (higher energy K components)

⇒ Wrong by a few MHz: ***data fit will still look good***
  - 6^{th}, 8^{th} order constants
- **Not all the literature is correct….**
  - Case of acetol

Analysis of Spectral Data

- Notion of **"Canned" analysis programs** ***MISLEADING***
- Many molecules pose real challenges
- Not always a **"Standard Hamiltonion"**

$$\mathbf{H_{eff} = H_{rot} + H_{SO} + H_{SS} + H_{SR} + H_{hf} + H_{eQq}}$$

-States with quartet multiplicity and higher

$\Rightarrow$ Higher order terms (Brown and Carrington)

- The problem children…

$\Rightarrow$ Species with ***internal rotors***

- Kleiner code (developed by Hougen group)
- Every molecule different (E state of acetol)

$\Rightarrow$ Species with ***Perturbing Excited States***

- Rotational Perturbations (Lefebvre-Brion and Field)

Spin-Electronic
$L_+S_- + L_-S_+$
S-Uncoupling
$J_+S_- + J_-S_+$
L-Uncoupling
$J_+L_- + J_-L_+$

Rotational Constants for Acetol (Ground State)

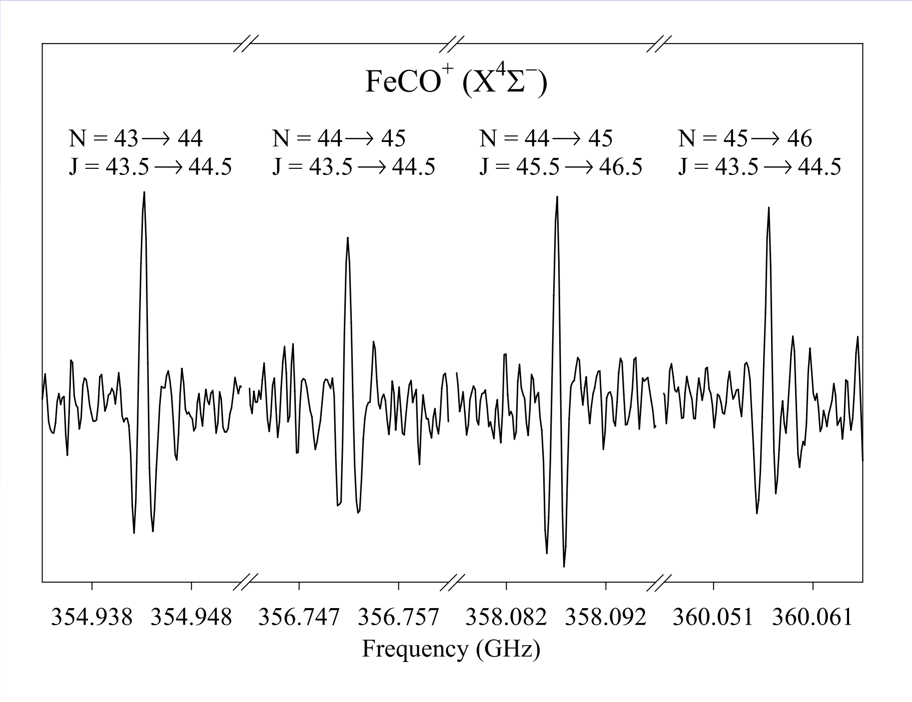
Subset of Spectroscopic Constants (47 Total):		Apponi et al. 2006	
Parameter	Operator	This Work	Kattija-Ari et al.
V_3	$(1/2)(1-\cos 3\gamma)$	67.839(34) cm^{-1}	68(4) cm-1
F	P_γ^2	164.084(53) GHz	157.931 fixed
ρ	$P_\gamma P_a$	0.055337(30) unitless	nd
A (diagonalized)	P_a^2	10013.53(61)	10069.410(57)
B (diagonalized)	P_b^2	3834.36(16)	3810.412(8)
C (diagonalized)	P_c^2	2911.04(12)	2864.883(4)
D_{ab}	$\{P_a,P_b\}$	1216.18(35)	nd
$\Delta I=I_a+I_b-I_c$		8.7 amu Å^2	6.4 amu Å^2
Total number of lines		1203	53
Microwave RMS		4 kHz	A-state 20 kHz
Millimeter wave RMS		54 kHz	E-state 9 MHz

$FeCO^+$ ($X^4\Sigma^-$)

- $H_{eff} = H_{rot} + H_{sr} + H_{ss} + H_{sr}^{(3)}$

$\Rightarrow H_{sr}^{(3)} = 6^{1/2}/10\ \gamma_s\ T^3(\mathbf{L}^2,\mathbf{N})\ T^3(\mathbf{S},\mathbf{S},\mathbf{S})$

- Fit to 57 kHz rms, but many higher order centrifugal distortion terms
- Lose ***predictive power***



Spectroscopic Constants (MHz)

B_0	3977.6472(26)
D_0	0.0015394(15)
H_0	$-5.52(27) \times 10^{-9}$
γ	3103.8(5.5)
γ_D	-0.38763(42)
γ_H	$2.340(15) \times 10^{-5}$
γ_L	$-8.25(21) \times 10^{-10}$
λ	131007(255)
λ_D	9.482(32)
λ_H	-0.0001702(32)
γ_s	-72.4(1.9)
γ_{sD}	0.09463(17)
γ_{sH}	$-5.534(56) \times 10^{-6}$
γ_{sL}	$1.237(77) \times 10^{-10}$

De-perturbation analysis

H_{eff} with perturbing $^2\Sigma$, $^4\Pi$, $^2\Pi$ states

In Conclusion…

- High resolution lab spectroscopy is DIFFICULT, COSTLY, DANGEROUS and PLAIN HARD WORK
- Not something that can be turned on and off at a moment's notice

- NOT all astrophysical spectroscopic problems have been solved

⇒ Many ***reactive species*** have never been studied

- Good interstellar candidates for U lines

⇒ Not clear that all ***claimed interstellar detections*** are correct

- Have a method for consistent identification
- Grossly mislead ourselves ***about contaminants*** in interstellar spectra

- ***High resolution spectroscopy*** is a formidable chemical technique

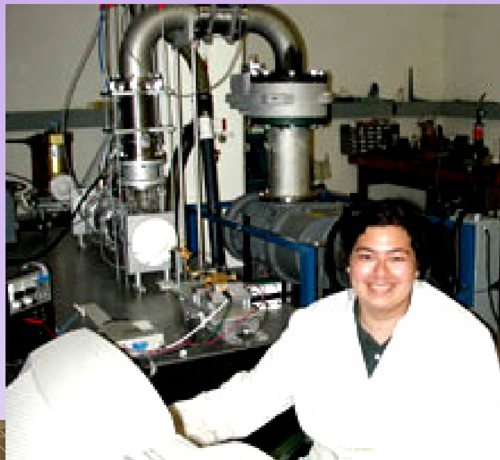
⇒ Derive accurate structures, bond lengths, bonding characteristics, orbital content, relativistic effects in quantum mechanics

- ***Astronomy only one application....and funding is required***

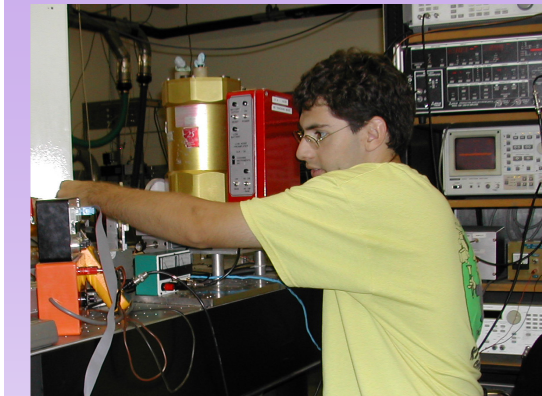
Hydrides/ Hydride Ions	Organic Species	Ions
SiH/SiH^+	$HOCH_2OH$	CCH^-
H_2DO^+	$HOCH_2NH_2$	CCH^+
MnH	HOCN	CN^+/CN^-
AlH^+	HOCH=CHOH	C_3H^+
NaH^+	NHCHO	$CH_3OH_2^+$
MgH^+	CH_3OCH	N_2OH^+
CD^+	CH_3OCH_2	NH_2CHOH^+
$^{13}CH^+$	$HC(OH)_2$	SiO^+
	HC_2OH_2	FeO^+
		$MgNC^+$
		$(CH_3)_2OH^+$
		$HC(OH)CH_3^+$

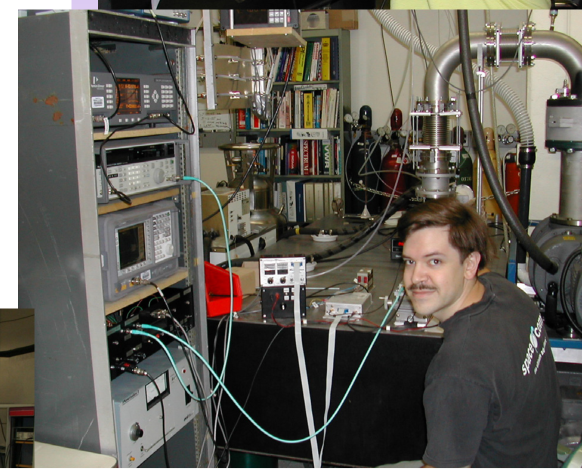
For the lab
- Greater availability of THz sources
- Source with more T. control
- More interested students !

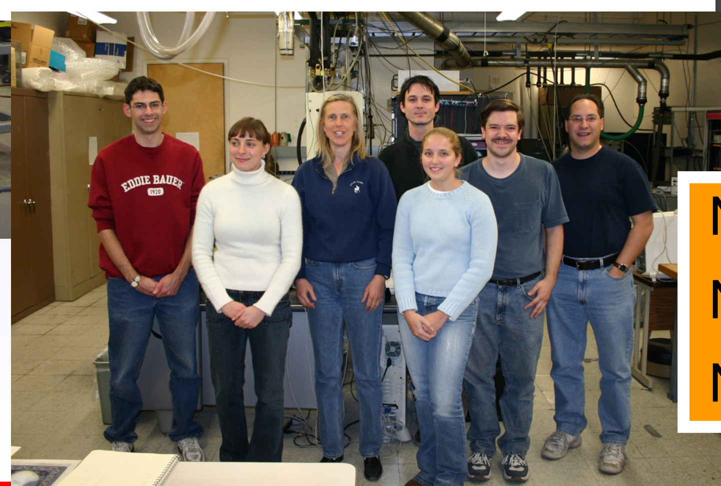
h no



And thanks to the Ziurys Group
Dr. Aldo Apponi
Dr. Chandra Savage
Dr. Alexandra Janczyk
Dr. DeWayne Halfen
Stefanie Milam
Mike Flory
Emmy Tenenbaum
Robin Pulliam
James Hoy
Shawn McLamarrah







NASA Lab Astrophysics
NASA Astrobiology
NSF Physical Chemistry

Arizona Radio Observatory