New THz Spectroscopic Tools for Laboratory Astrochemistry

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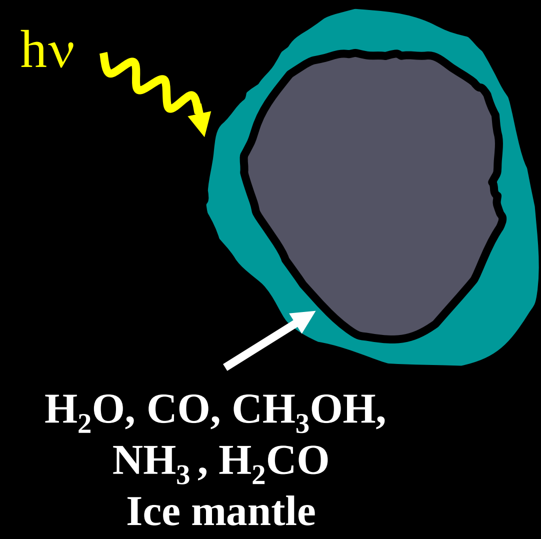
Motivation: Understanding COMs in the ISM

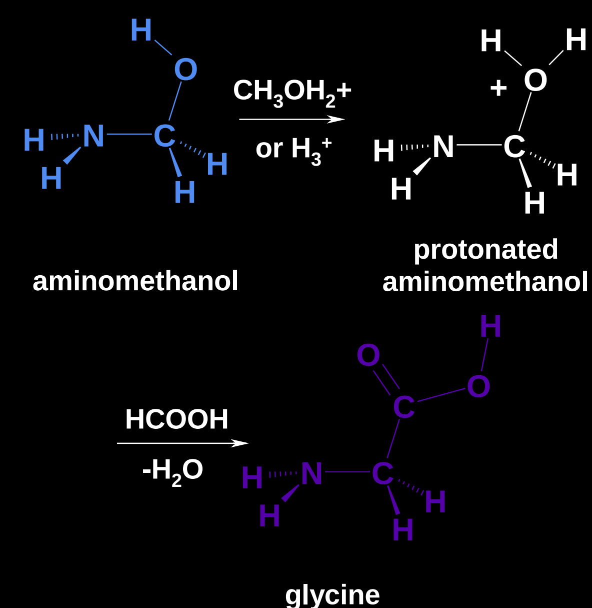
Grain surface formation

- Simple molecules form in ice via single-atom addition reactions
- Organic radicals form in ice via photolysis of simple molecules
- Radicals react during warm-up to form larger organics



Gas phase formation

- Molecules are released from ices
- Gas-phase molecules are ionized
- Ion-molecule reactions drive gas-phase organic chemistry



Transient molecules are the driving forces for both grain-surface and gas-phase chemistry.

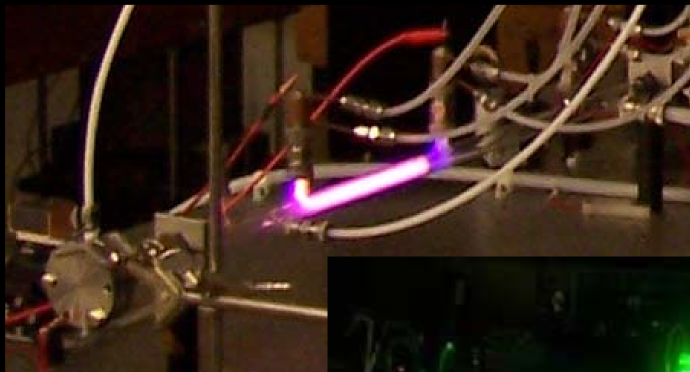
2 atoms	3 atoms	4 atoms	5 atoms	6 atoms	7 atoms	8 atoms	9 atoms	10 atoms	11 atoms	12 atoms	13 atoms
H_2	C_3	c-C_3H	C_5	C_5H	C_6H	CH_3C_3N	CH_3C_4H	CH_3C_5N	HC_9N	C_6H_6	$HC_{11}N$
AlF	C_2H	l-C_3H	C_4H	l-H_2C_4	CH_2CHCN	HC(O)OCH_3	CH_3CH_2CN	$(CH_3)_2CO$	CH_3C_6H	$C_2H_5OCH_3$	
AlCl	C_2O	C_3N	C_4Si	C_2H_4	CH_3C_2H	CH_3COOH	$(CH_3)_2O$	$(CH_2OH)_2$			
C_2	C_2S	C_3O	l-C_3H_2	CH_3CN	HC_5N	C_7H	CH_3CH_2OH	CH_3CH_2CHO			
CH	CH_2	C_3S	c-C_3H_2	CH_3NC	CH_3CHO	H_2C_6	HC_7N				
CH^+	HCN	C_2H_2	H_2CCN	CH_3OH	CH_3NH_2	CH_2OHCHO	C_8H				
CN	HCO	NH_3	CH_4	CH_3SH	c-C_2H_4O	l-HC_6H	$CH_3C(O)NH_2$				
CO	HCO^+	HCCN	HC_3N	HC_3NH^+	H_2CCHOH	CH_2CHCHO	C_8H^-				
CO^+	HCS^+	$HCNH^+$	HC_2NC	HC_2CHO	C_6H^-	CH_2CCHCN	C_3H_6				
CP	HOC^+	HNCO	HCOOH	NH_2CHO							
SiC	H_2O	HNCS	H_2CNH	C_5N							
HCl	H_2S	$HOCO^+$	H_2C_2O	l-HC_4H							
KCl	HNC	H_2CO	H_2NCN	l-HC_4N							
NH	HNO	H_2CN	HNC_3	c-H_2C_3O							
NO	MgCN	H_2CS	SiH_4	H_2CCNH							
NS	MgNC	H_3O^+	H_2COH^+								
NaCl	N_2H^+	c-SiC_3	C_4H^-								
OH	N_2O	CH_3									
PN	NaCN										
SO	OCS										
SO^+	SO_2										
SiN	c-SiC_2										
SiO	CO_2										
SiS	NH_2										
CS	H_3^+										
HF	H_2D^+, HD_2^+										
SH	SiCN										
HD	AlNC										
FeO	SiNC										
O_2	HCP										
CF^+											
SiH											
PO											

Detected Interstellar Molecules

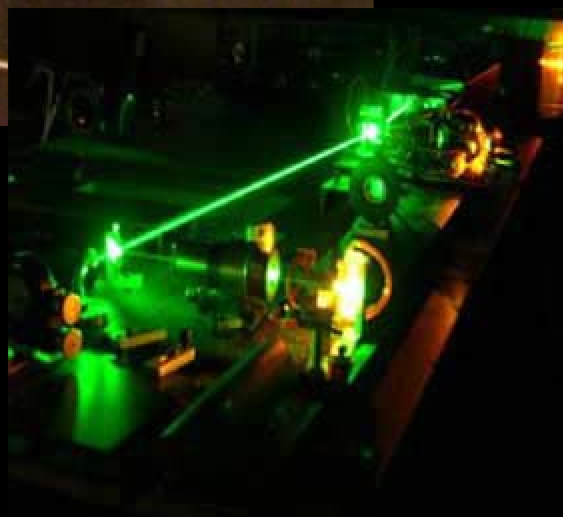
~40% are Radicals and Ions

Production Methods

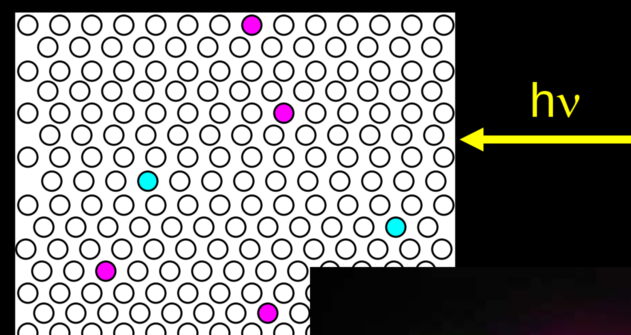
- Small quantities (low efficiency)
- High temperatures = weak signals
- Interference from stable molecules
- Reactivity/instability of products



Discharges



Photolysis



Matrix Isolation

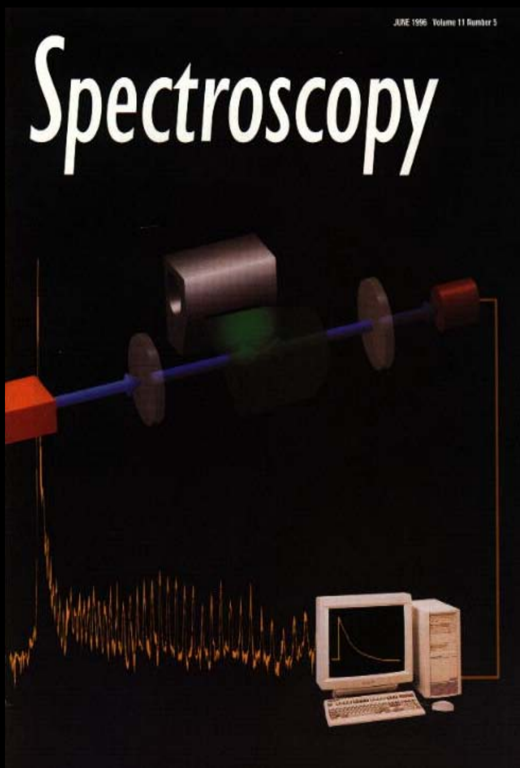
Supersonic Expansions

High-Sensitivity Cavity-Enhanced Spectroscopy

Fabry–Perot cavity pulsed Fourier transform microwave spectrometer with a pulsed nozzle particle source

T. J. Balle and W. H. Flygare
Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801
(Received 28 July 1980; accepted for publication 12 September 1980)

~2 – 50 GHz

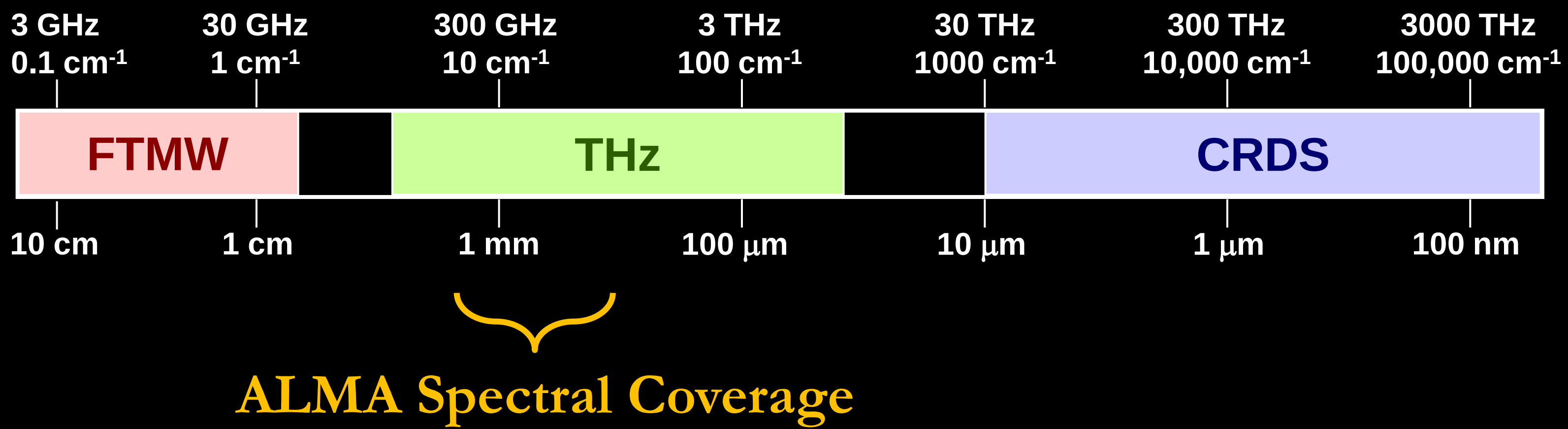


> 1000 cm^{-1}

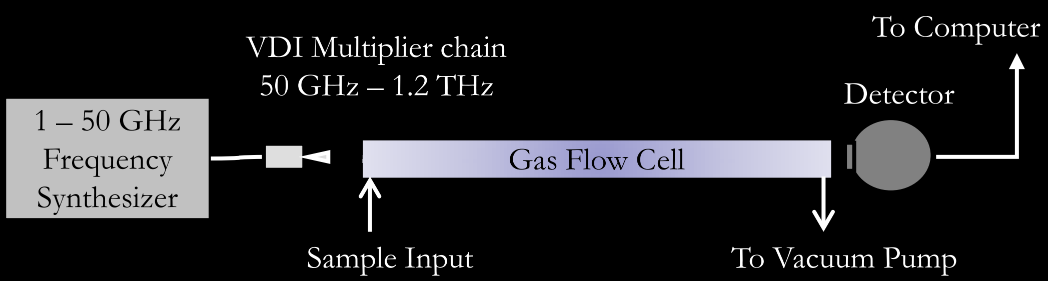
Cavity ring-down optical spectrometer for absorption measurements using pulsed laser sources

Anthony O'Keefe and David A.G. Deacon
Deacon Research, 900 Welch Rd., Palo Alto, CA 94304
Review of Scientific Instruments, 59, 2544 (1988)

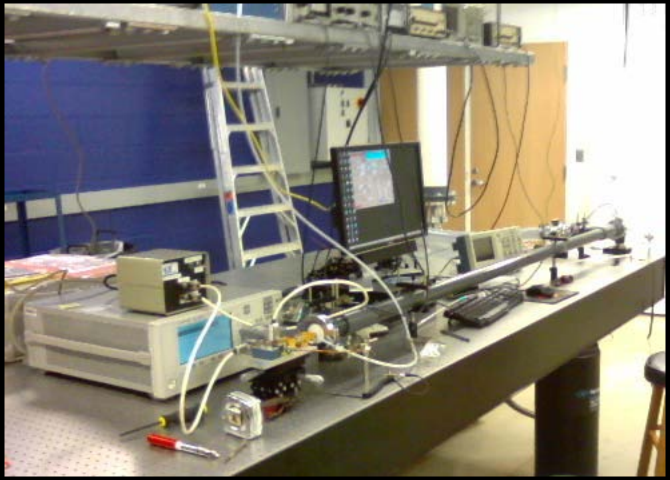
The 'THz Gap'

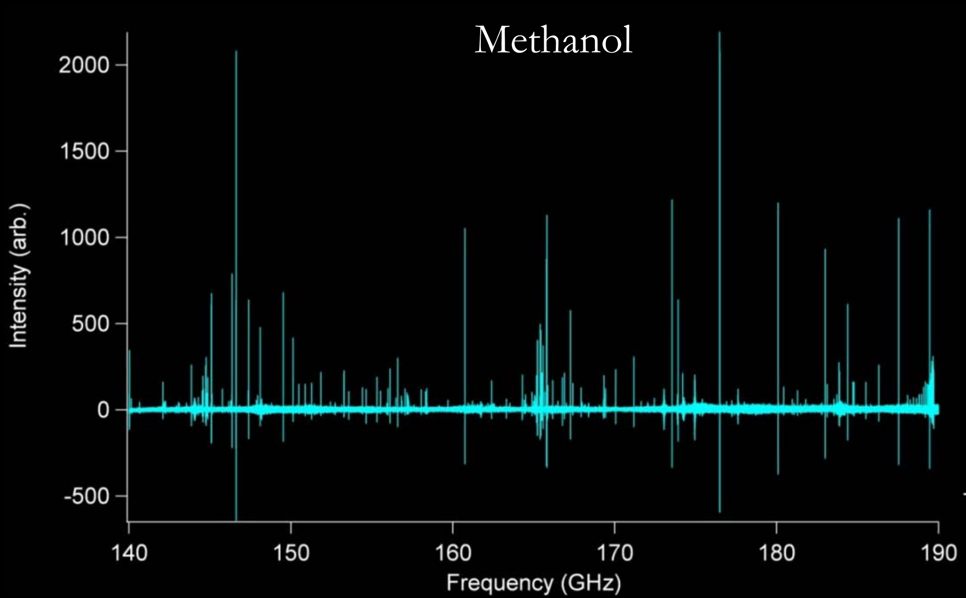

3 GHz
0.1 cm-1
30 GHz
1 cm-1
300 GHz
10 cm-1
3 THz
100 cm-1
30 THz
1000 cm-1
300 THz
10,000 cm-1
3000 THz
100,000 cm-1
FTMW
THz
CRDS
10 cm
1 cm
1 mm
100 μm
10 μm
1 μm
100 nm
ALMA Spectral Coverage

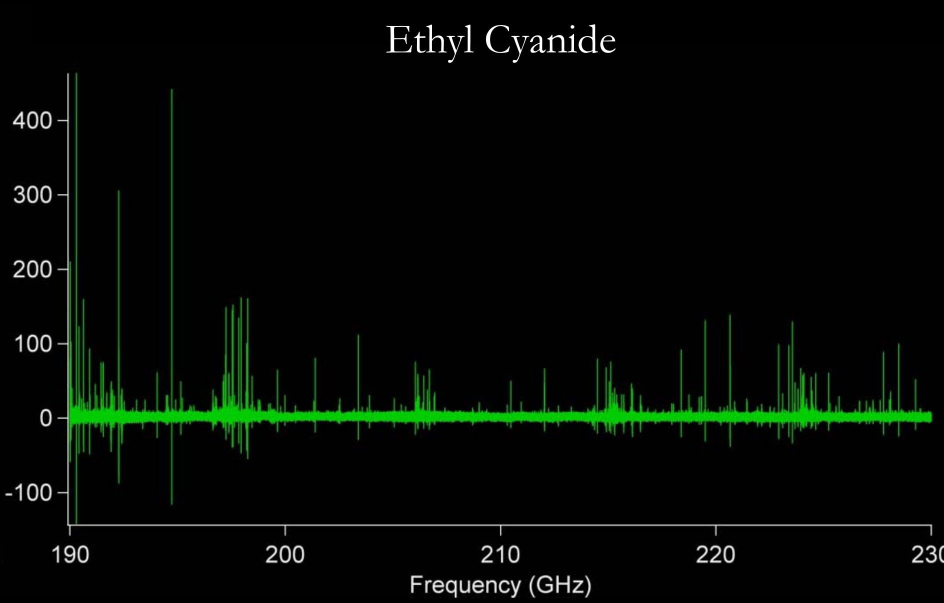
Laboratory Spectral Cataloging



First light April 1, 2009!

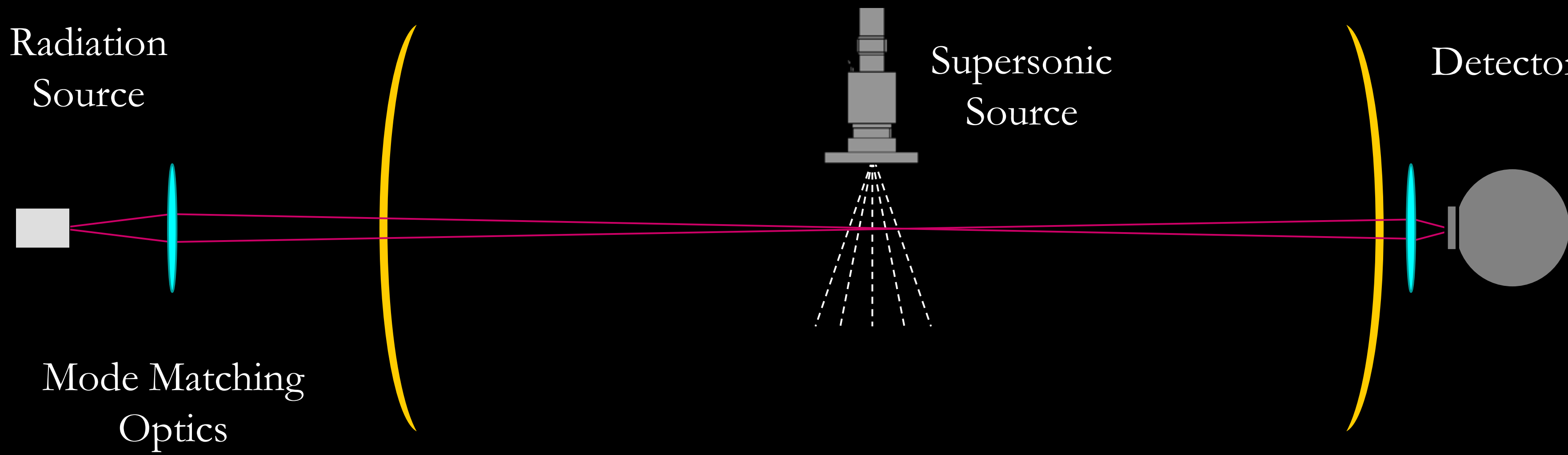


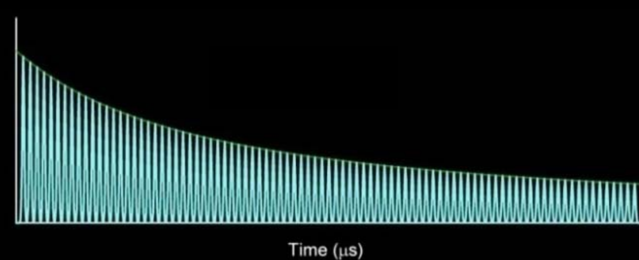




CRDS High Finesse Cavity

R = 99.99%



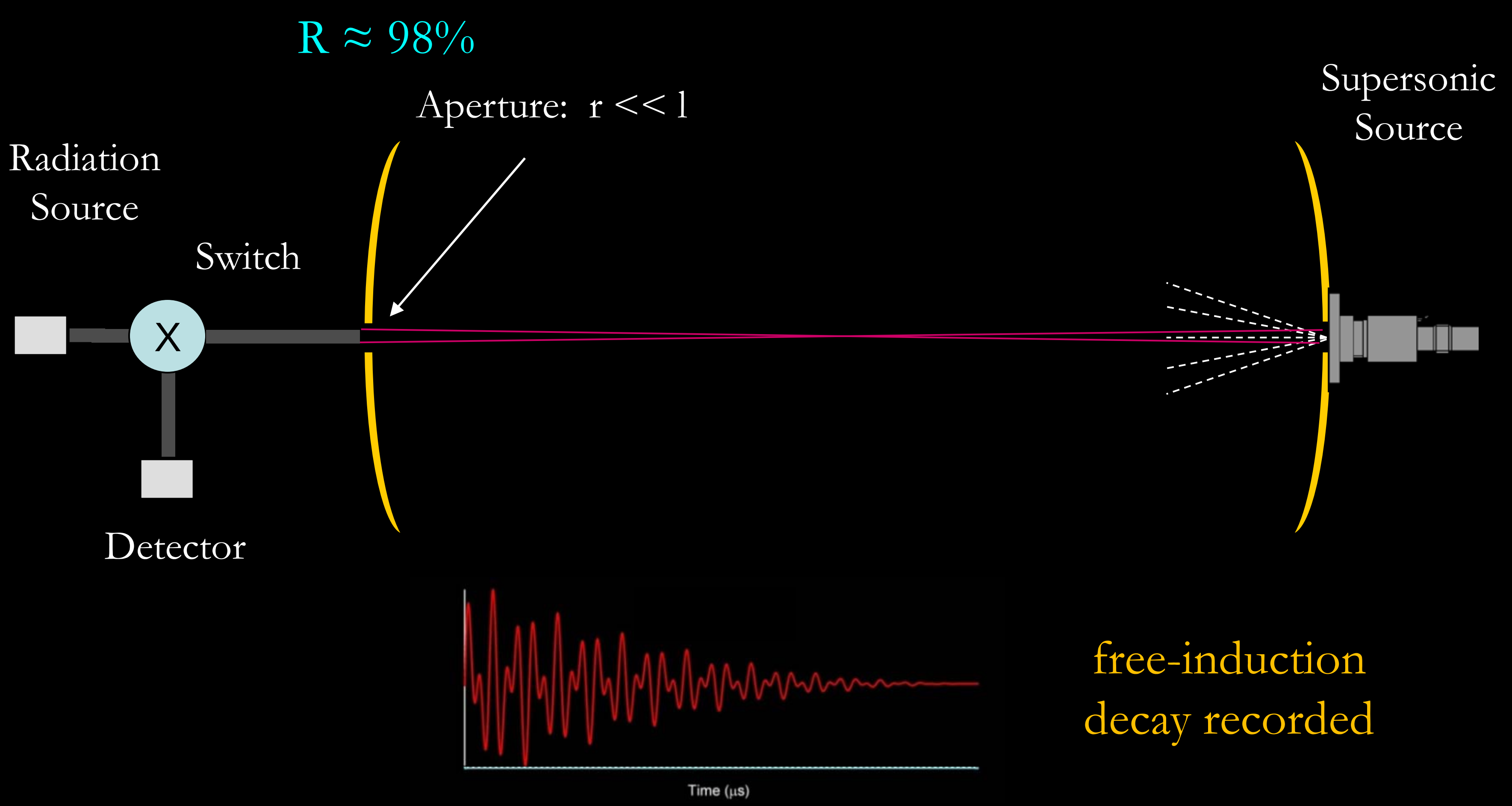


cavity ringdown recorded

IR mirrors → dielectric coated
Losses due to transmission

THz mirrors → metal coated
Losses due to skin depth

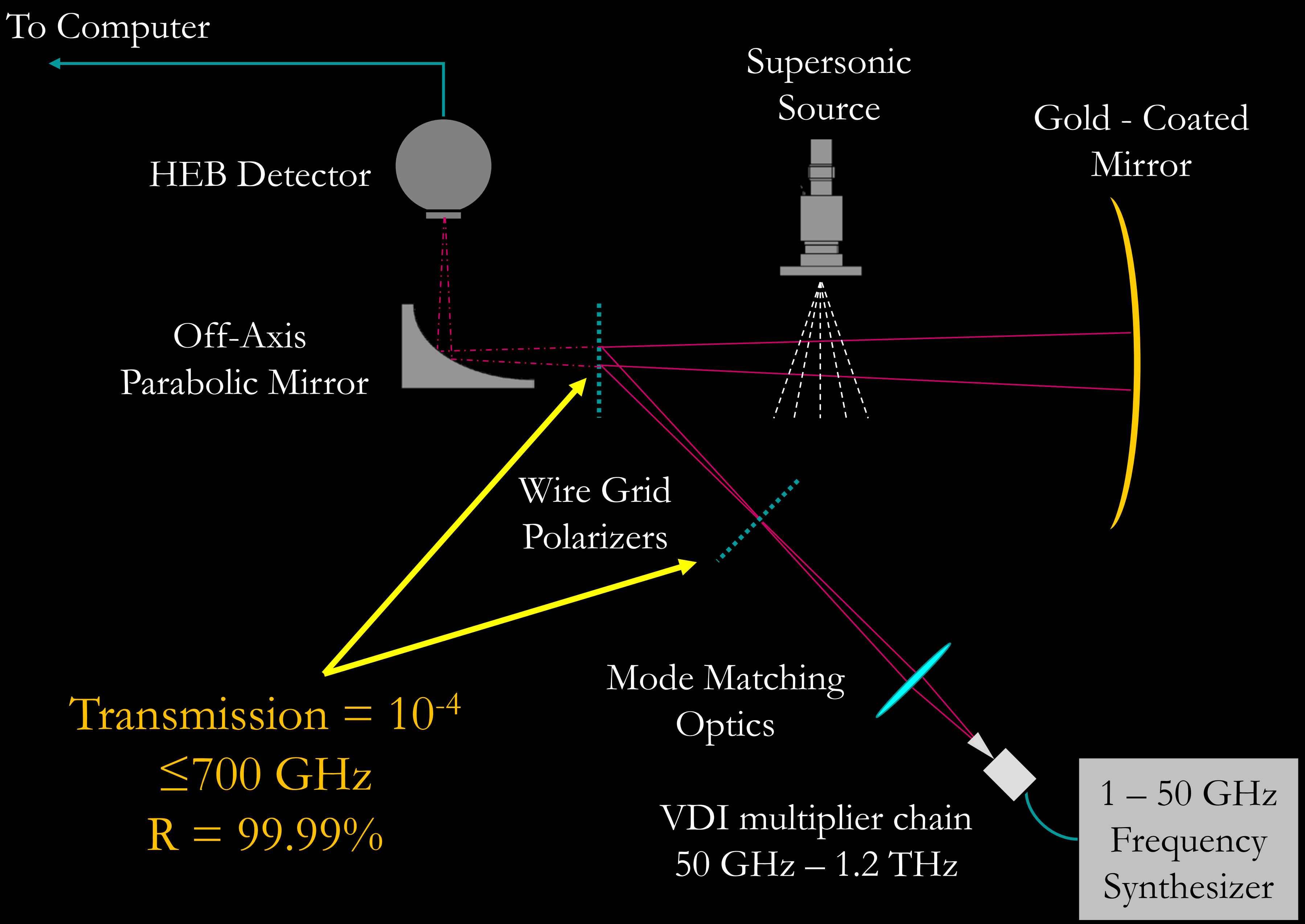
FTMW High Finesse Cavity



microwave mirrors → aperture
Large λ, small losses

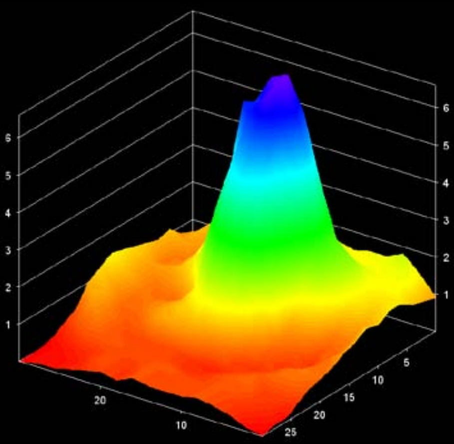
THz mirrors → ?
Small λ, large losses with any aperture!

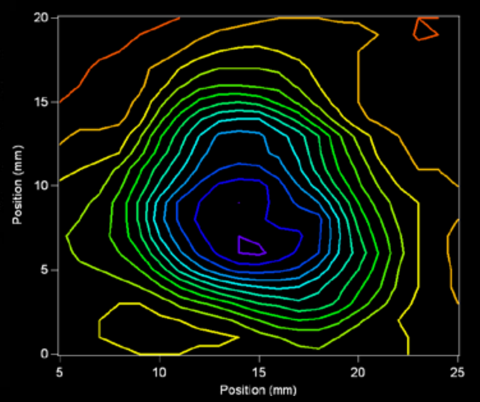
Proposed THz-CRDS Spectrometer



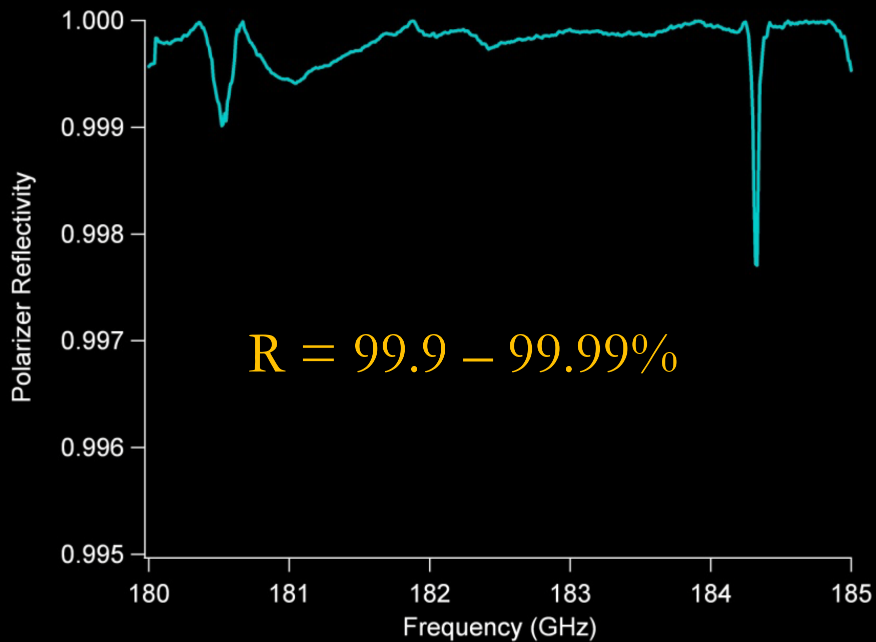
Progress Toward THz-CRDS

Beam profiling completed,
mode-matching calculations performed





Polarizer reflectivity
tested up to 300 GHz



Progress Toward THz-CRDS

Benchtop optics setup completed

Next Steps:

- Finish bench-top cavity tests: requires QMC HEB detector (expected to ship next week)
- Place cavity in vacuum chamber
- Test fully-integrated system
- Begin molecular spectroscopy
- Extend system to higher frequencies
- Extend concept to broadband spectral acquisition

Future Work: FT-THz Spectroscopy

Similar cavity setup to THz-CRDS

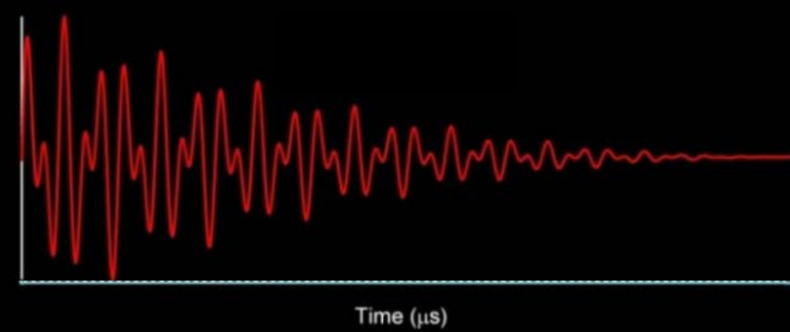
Sample is polarized with high-power radiation pulse, FID recorded

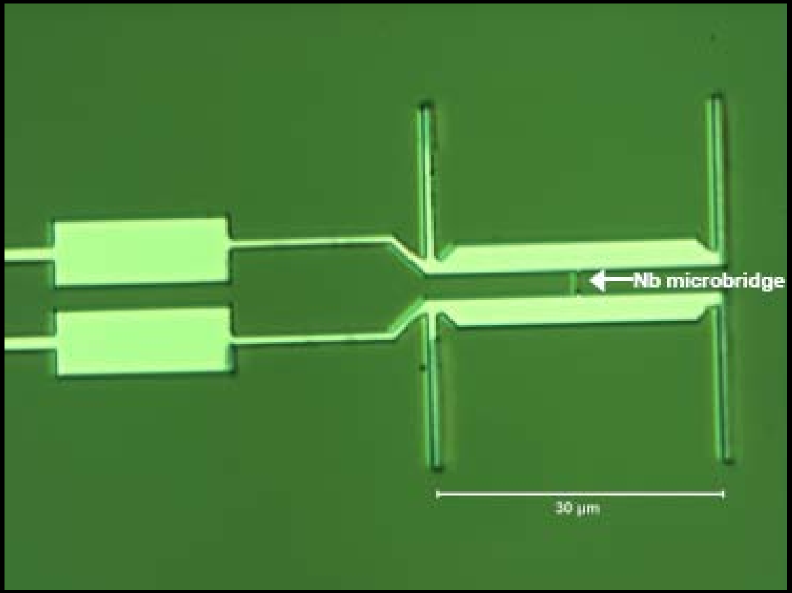
Lower mirror R required: Optics are less demanding, modes are broader than CRDS

Hardware requirements are beyond current (commercially) available technology:

- Nb HEB heterodyne detector (can be custom-built by Prober group)

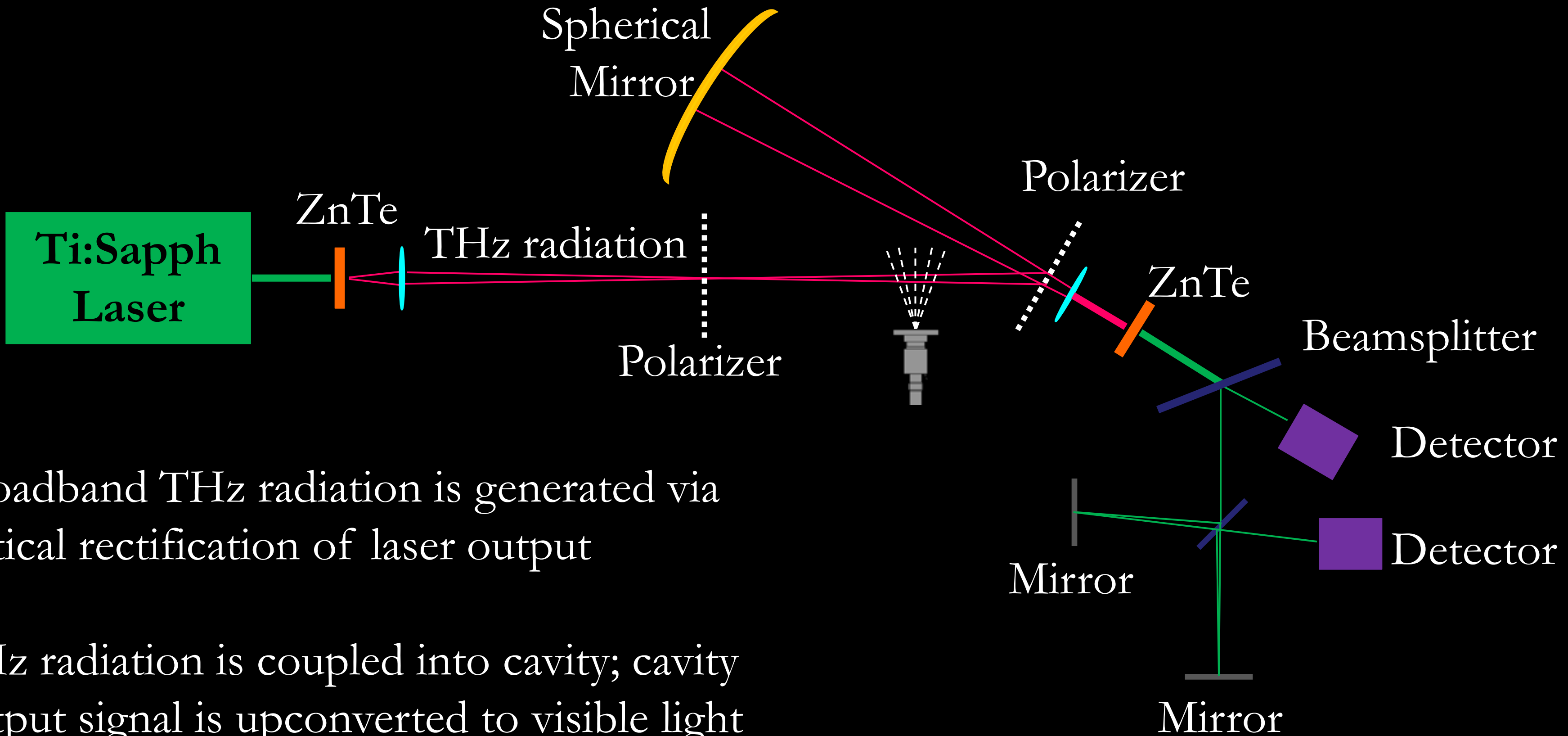
- Higher power amplifiers at higher frequencies (none commercially available; spare Herschel amps??)





In collaboration with Geoff Blake at Caltech and Dan Prober at Yale

Future Work: TD-THz-CRDS



- Broadband THz radiation is generated via optical rectification of laser output
- THz radiation is coupled into cavity; cavity output signal is upconverted to visible light
- Ringdown signal is monitored directly
- Second beam is coupled into interferometer; time-dependence of ringdown is monitored
- Broadband frequency spectrum is deconvolved

In collaboration with Tim Lian and Brian Dyer at Emory

Using THz Spectroscopy to Trace Prebiotic Chemistry in Space

What do we plan to measure?

- Photolysis branching ratios for complex organics
- Spectra of small, reactive organics produced via $O(^1D)$ insertion
- Spectra of molecular ions with complex internal motion
- THz spectral catalogs of “interstellar weeds”

Acknowledgements

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