Terahertz Spectroscopy Comes of Age

Mark Sherwin

Director, Institute for Terahertz Science and Technology

THz – Brief History

Volume I. *July–August, 1893.* *Number 1.*

THE

PHYSICAL REVIEW.

A STUDY OF THE TRANSMISSION SPECTRA OF CERTAIN SUBSTANCES IN THE INFRA-RED.

BY ERNEST F. NICHOLS.

WITHIN a few years the study of obscure radiation has been greatly advanced by systematic inquiry into the laws of dispersion of the infra-red rays by Langley,[1] Rubens,[2] Rubens and Snow,[3] and others. Along with this advancement has come

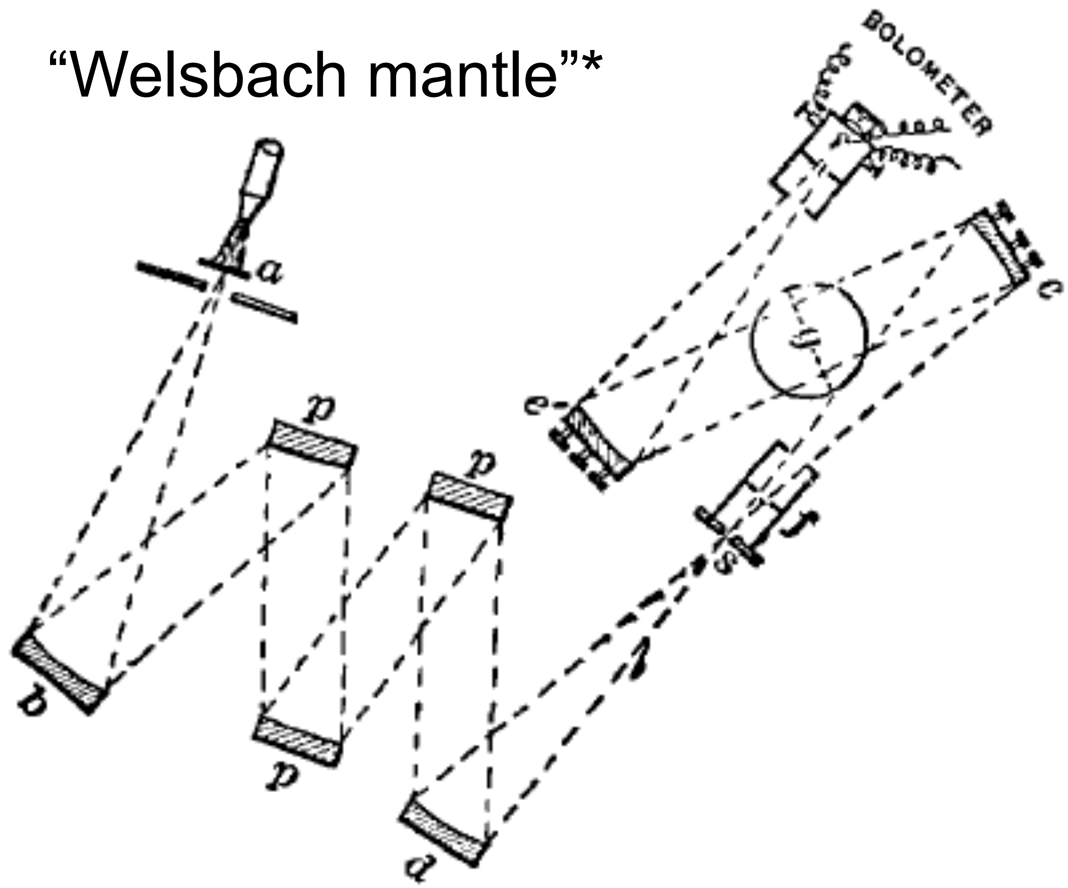
After Nichols left Berlin, Rubens continued the work, and in 1900 he isolated wavelengths of 6THz (50 microns) and made careful measurements which he gave to Max Planck who derived the Radiation Law. **Planck wrote in 1922 "Without the intervention of Rubens the formulation of the radiation law, and consequently the formulation of quantum theory would have taken place in a totally different manner, and perhaps even not at all in Germany".**

From talk by G. Williams

Terahertz (Far-Infrared) spectroscopy *ca* 1910

H. Rubens--Berlin

“Welsbach mantle”*



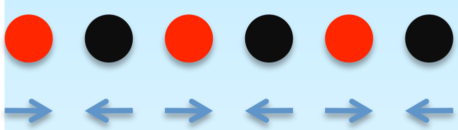
(b)

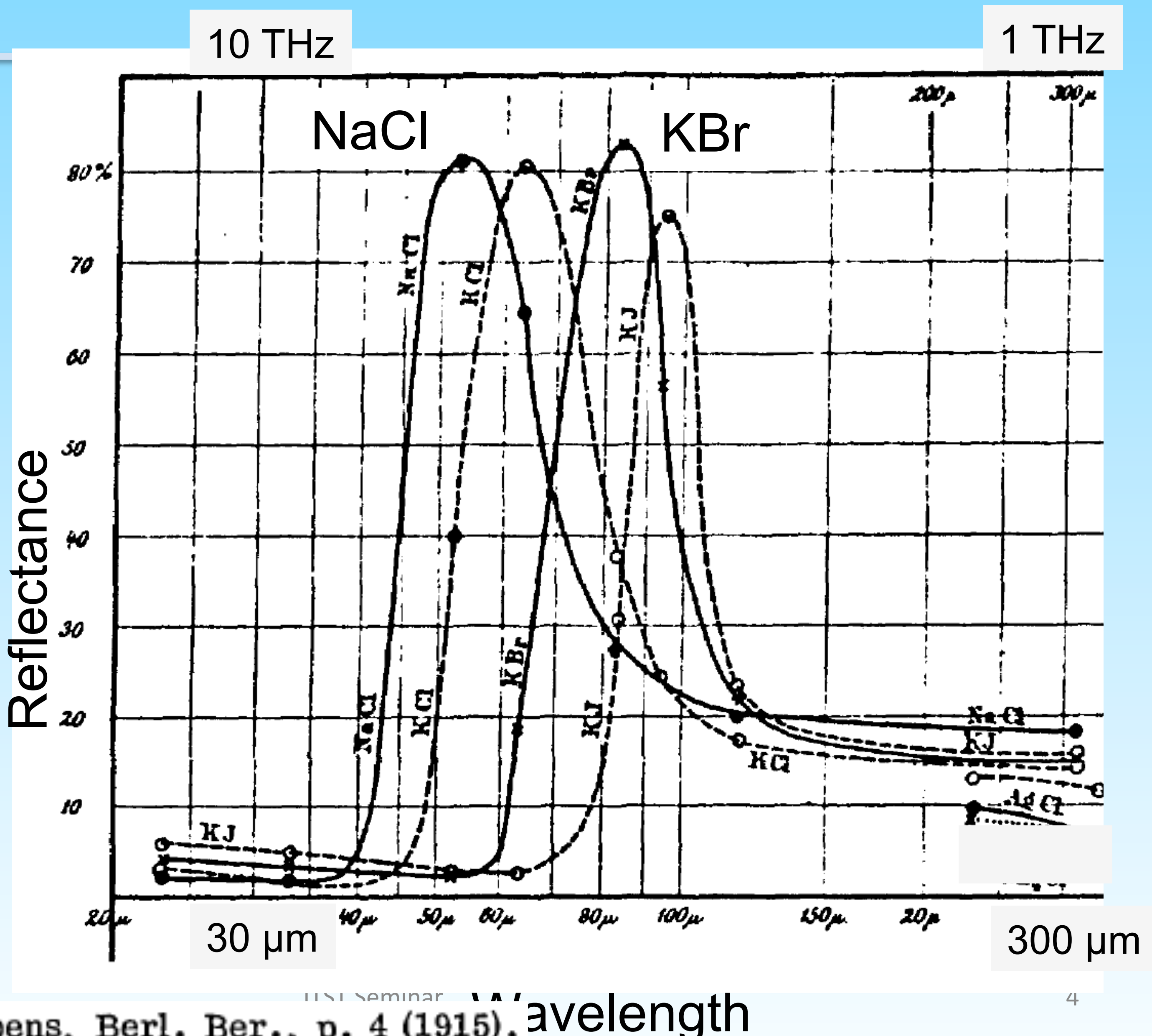
*rare-earth oxide in gas flame

See E. D. Palik, J. Opt. Soc. Am., Vol. 67, No. 7, July 1977

"Reststrahlen" bands of Alkali Halides

- Optical phonons

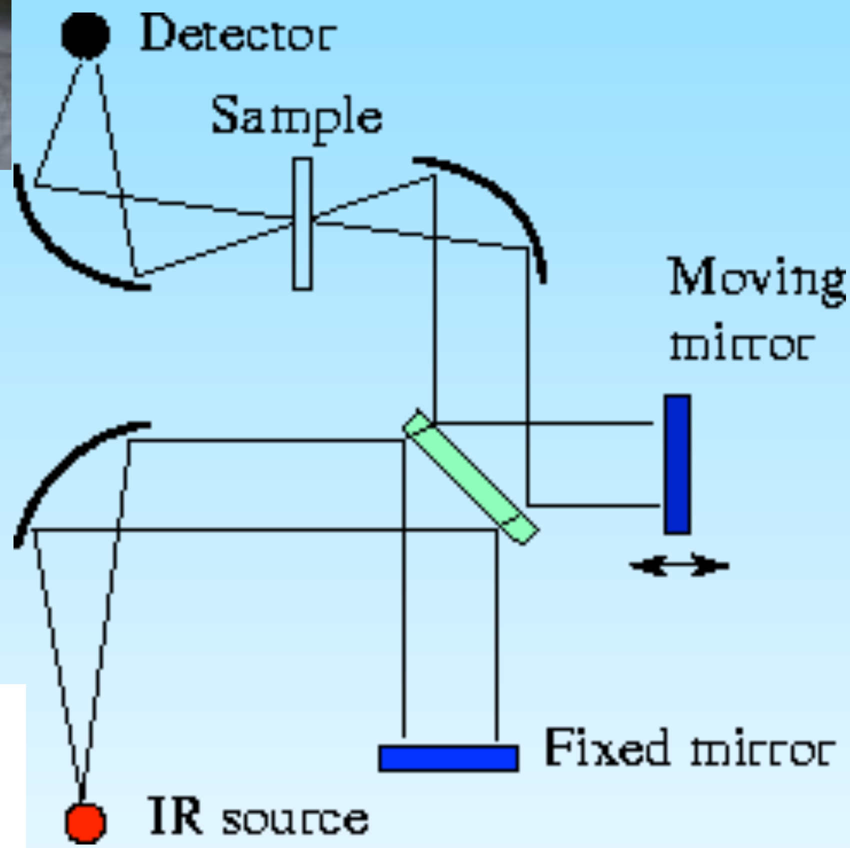




[13] H. Rubens, Berl. Ber., p. 4 (1915).

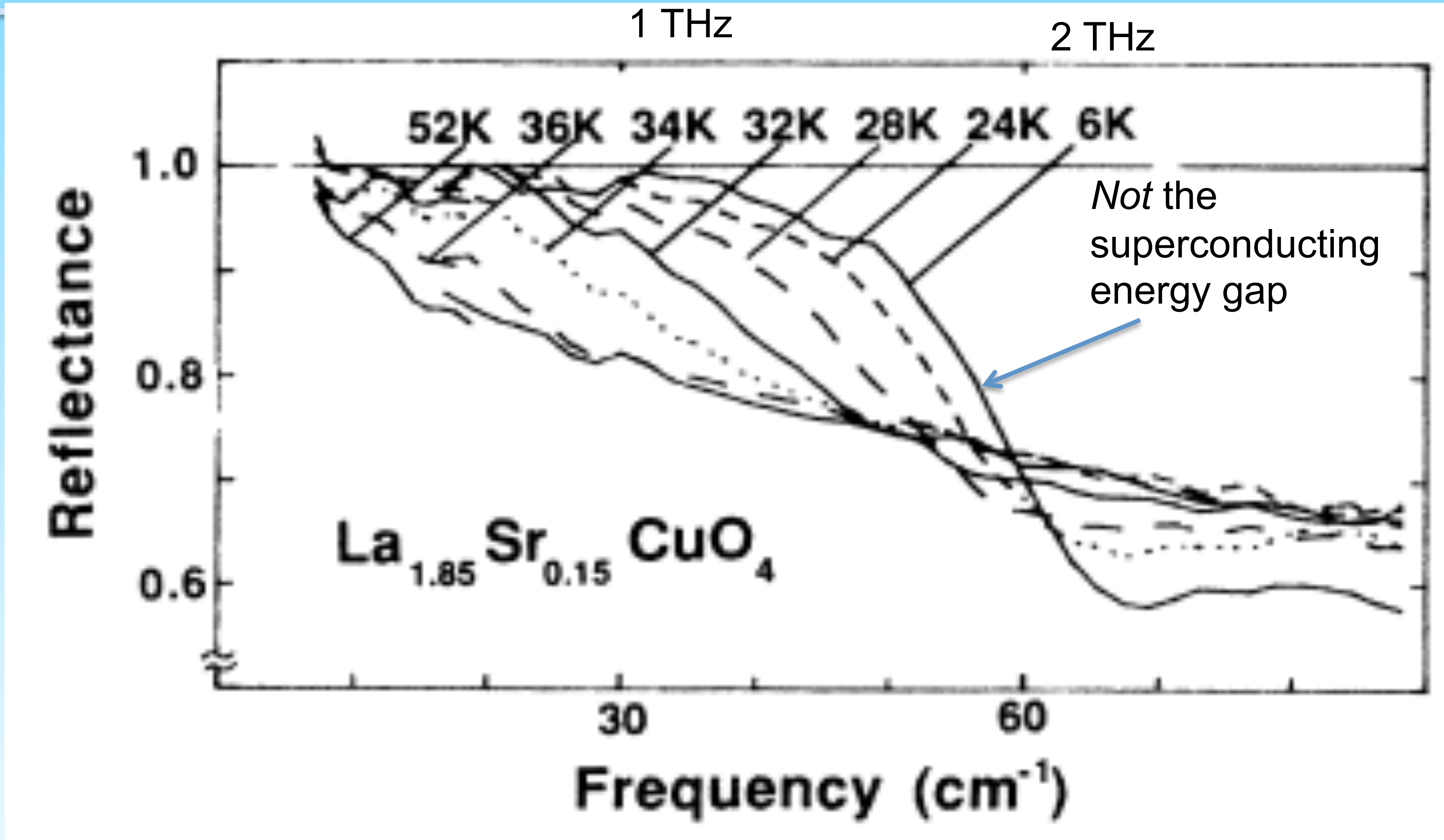
Fourier-Transform IR spectrometer

Liquid
He-cooled bolometer



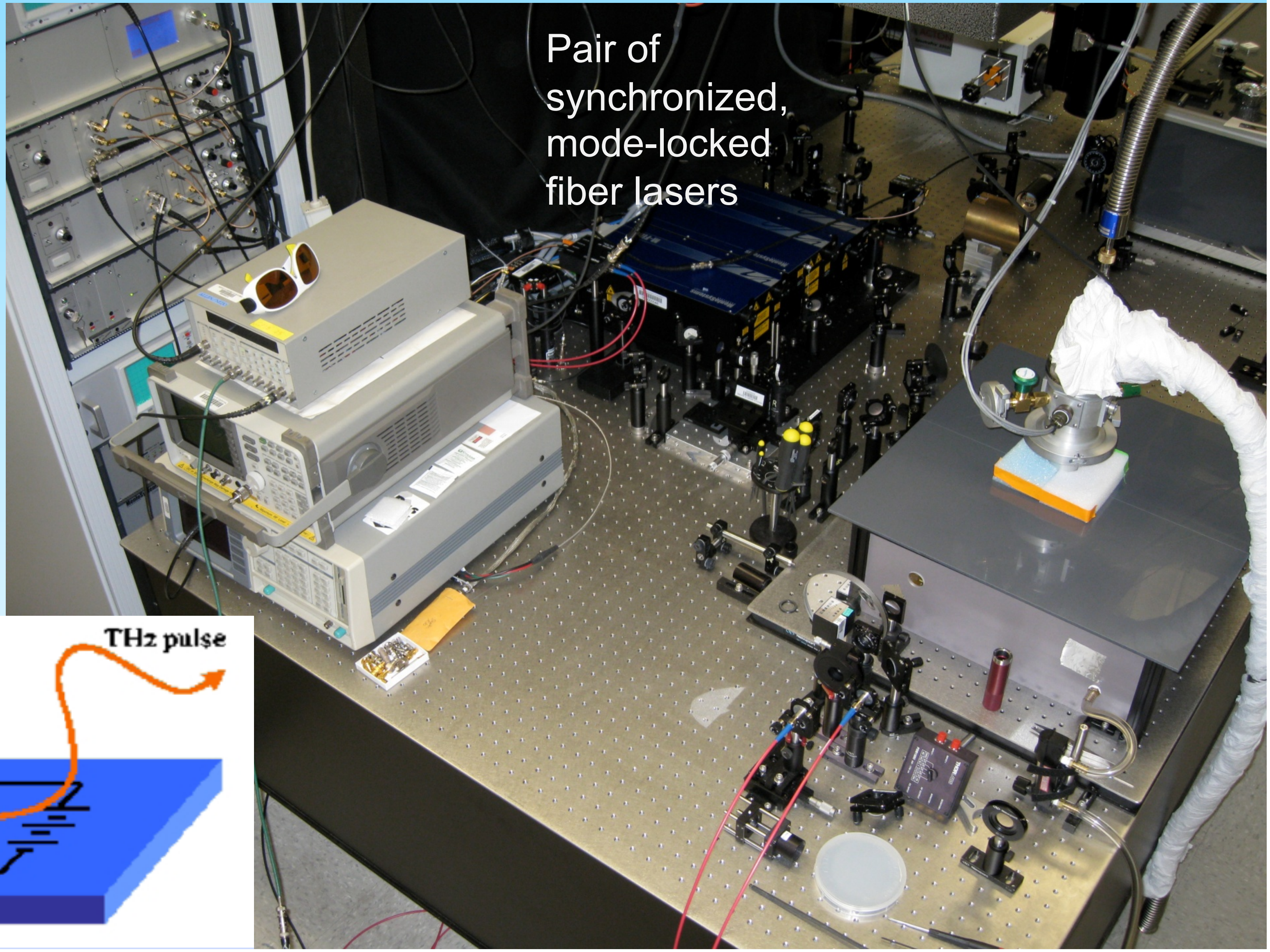
Mercury arc lamp

Reflectance of high-T_c superconductor

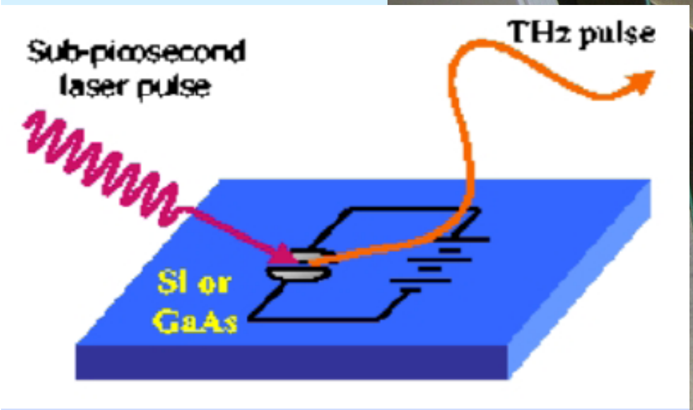


Sherwin, Richards and Zettl, Phys. Rev. B. **37**, 1587 (1988)

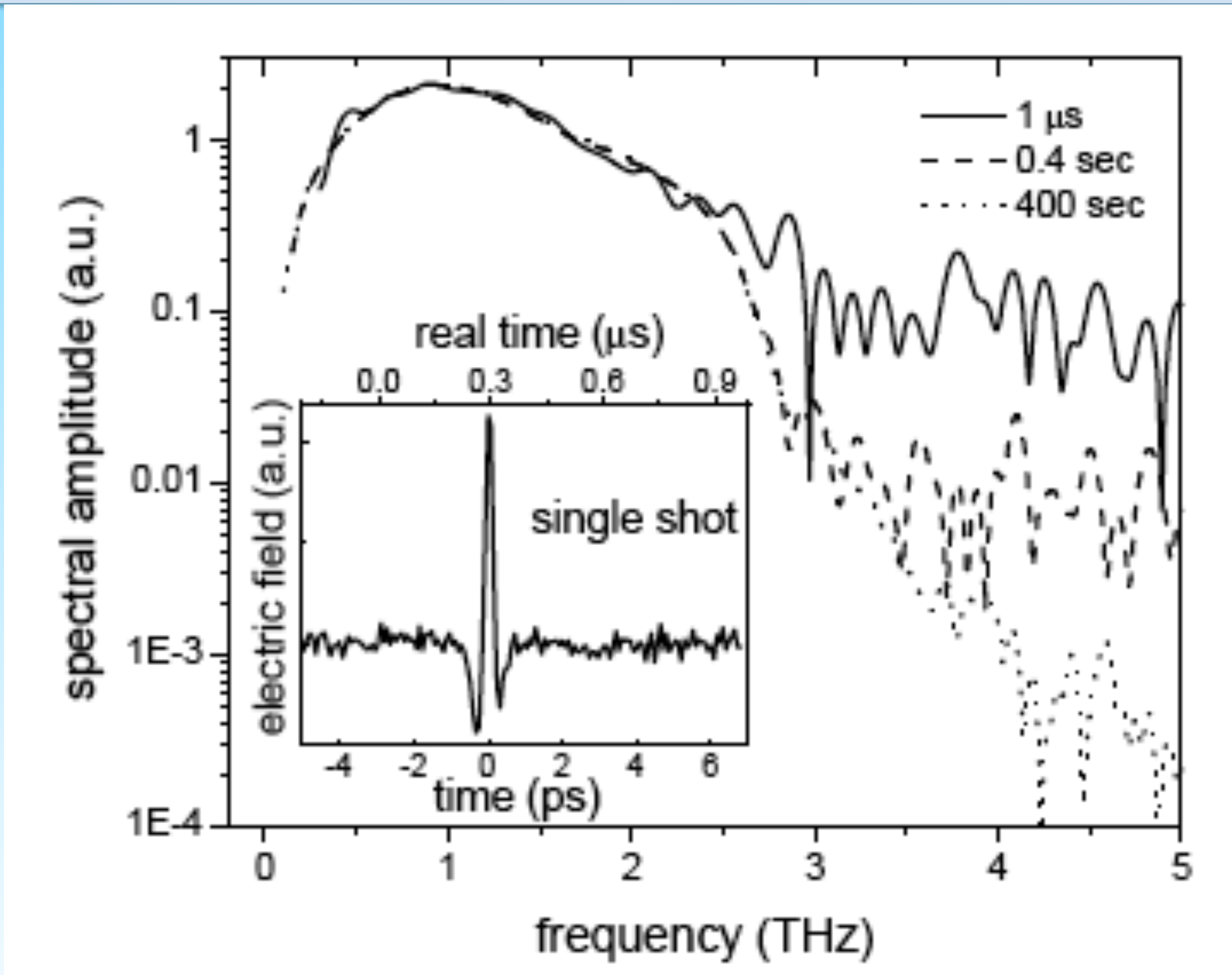
23 years later—
ITST video-rate THz spectrometer



"Auston switch"

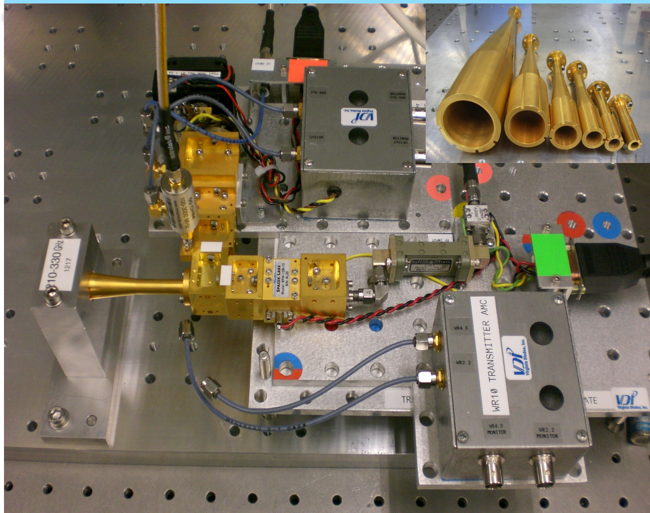


Acquire spectrum in 1 μs!

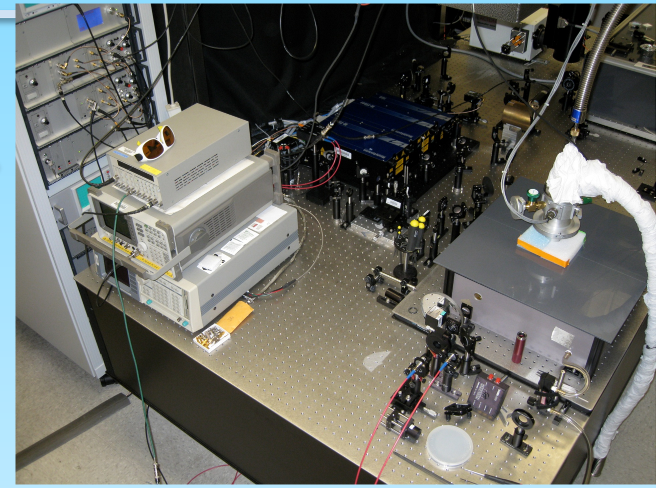


D. Stehr, C. M. Morris, C. Schmidt & MSS, Optics Lett., forthcoming

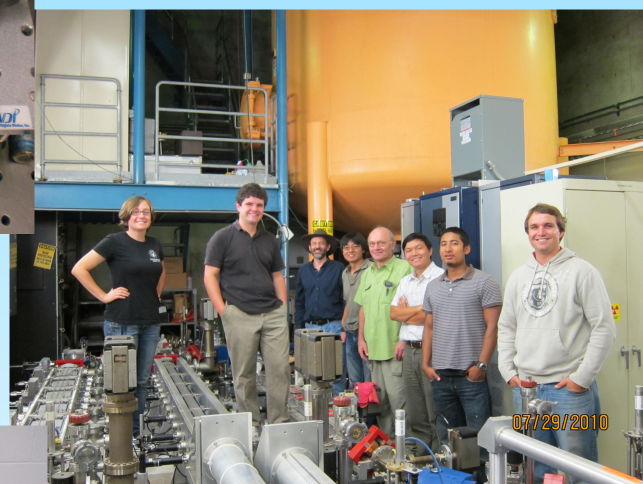
ITST THz sources and systems



Video-rate time-domain vector spectrometer
0.3-3 THz

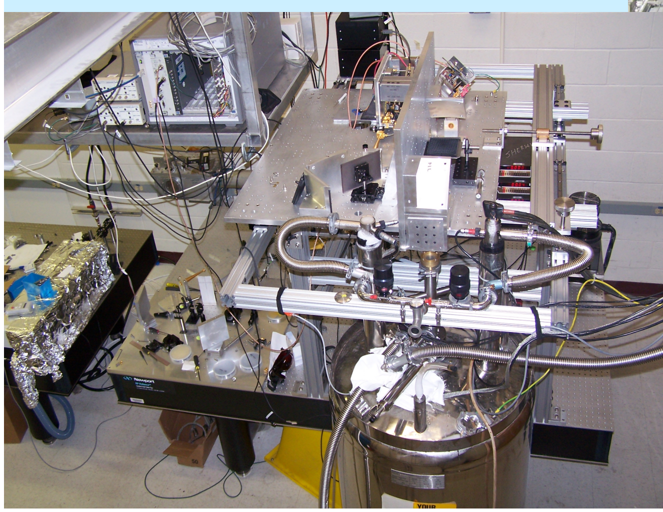


Frequency-domain vector spectrometer
0.07-0.7 THz



FTIR spectrometer
~1-100 THz

UCSB FELs
0.1-4.8 THz, kW power



cw and pulsed EPR
0.24 THz

Terahertz technology has come a long way!!

<u>Oct. 14</u> **Louis-Claude Brunel,** ITST
Pulsed EPR (ESR) in the THz Frequency Range and NanoSecond Time Scale

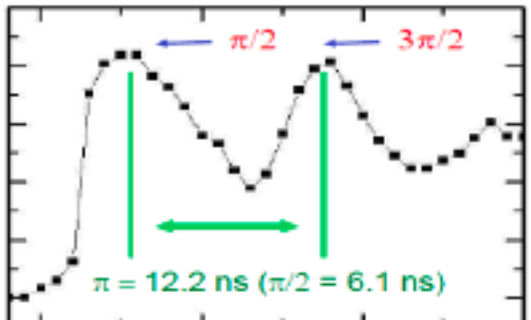
<u>Oct. 21</u> **Sascha Preu,** MRL –ITST
A broadly tunable THz source based on photomixing in "n-i-pn-i-p" superlattices

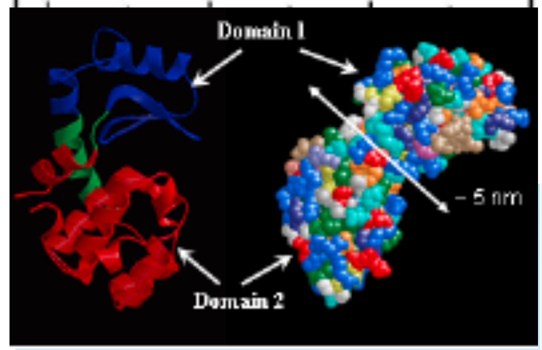
<u>Oct. 28</u> **Vinh Nguyen,** ITST
Probing the dynamics of biomolecules in liquid water by terahertz spectroscopy

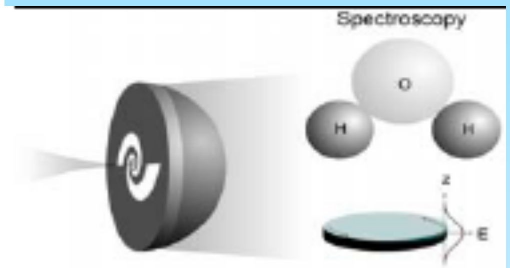
<u>Nov. 4</u> **Mark Rodwell,** ECE
Design of THz Field-Effect Transistors

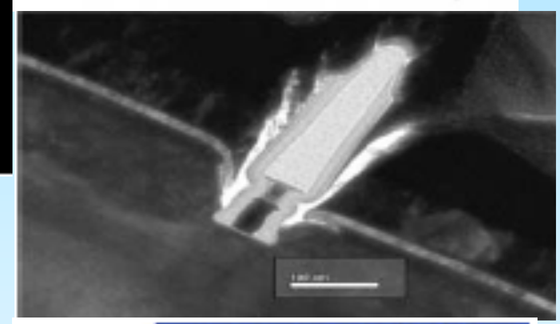
<u>Nov 18</u> **Songi Han,** Chem & BioChem, ITST
Electron Spin-Amplified Nuclear Magnetic Resonance at High Fields.

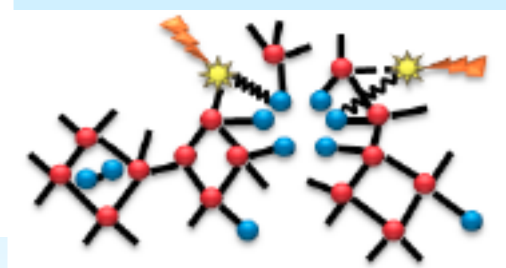
<u>Dec. 2</u> **Susanne Stemmer,** Materials
High-mobility complex oxide heterostructures by MBE

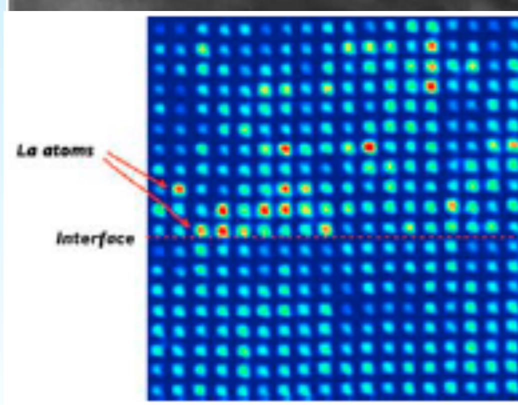












Outline

- Pulsed EPR at 0.24 THz
- Frequency-domain vector spectroscopy
- Nonlinear spectroscopy

Recent and ongoing research

- Pulsed EPR at 0.24 THz
  - N-V centers in diamond
  - Structure and dynamics of spin-labeled proteins
  - Light-induced EPR in organic solar cell material
- Frequency-domain vector spectroscopy
- Nonlinear spectroscopy

Recent and ongoing research

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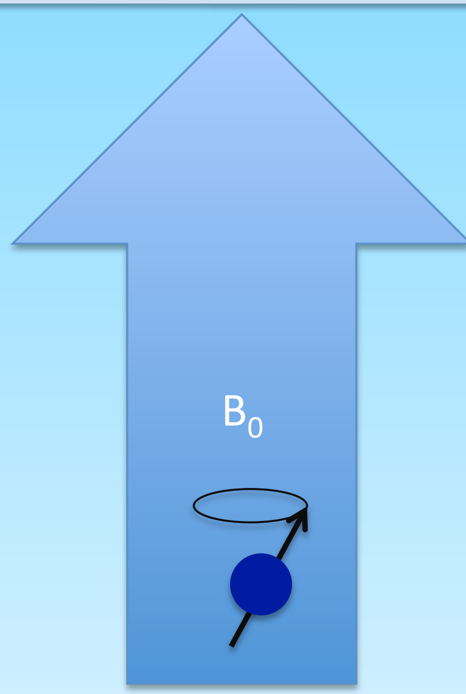
Precession in constant B



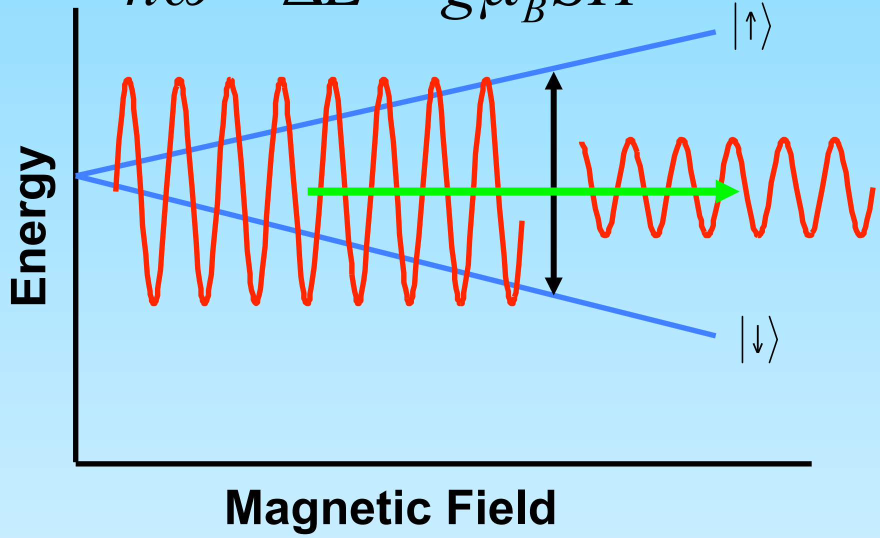
Spin-1/2 electron: $\frac{\gamma}{2\pi} = 28\ \text{GHz/Tesla}$

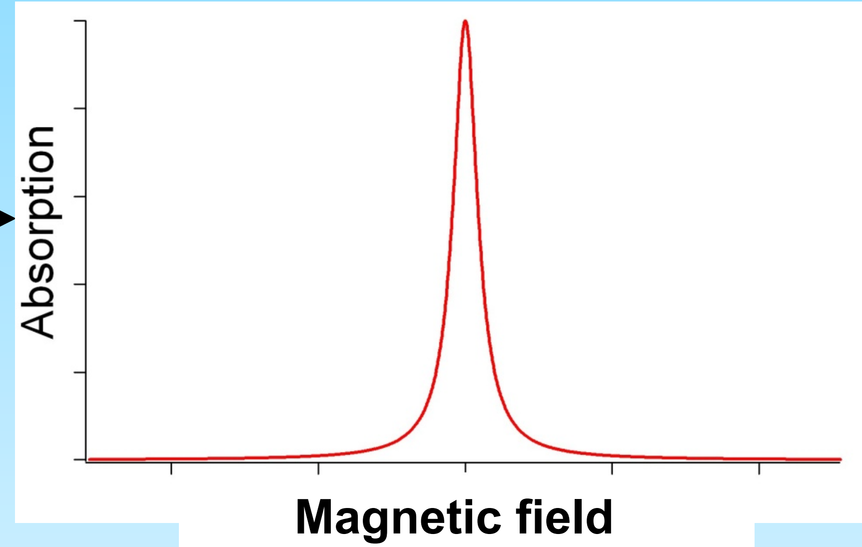
So 20 T->0.56 THz

Electron paramagnetic resonance (EPR)

Electron spin states split in magnetic field

$$\hbar\omega = \Delta E = g\mu_B SH$$





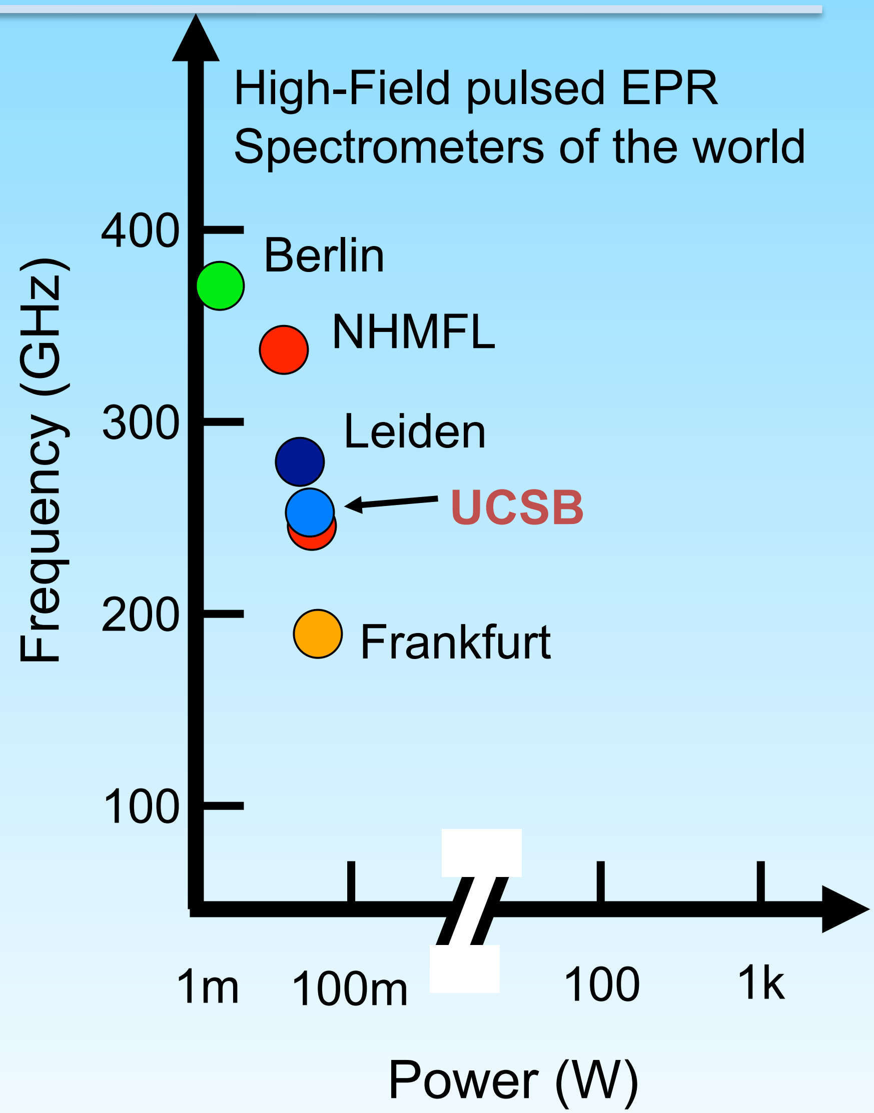
- Study local environment near unpaired electron
  - Orientationally dependent g-values
  - Number of spins
  - Other spins (Electrons and Nuclei) nearby
- Usually f=10 GHz (B=0.35 T)

Advantages of high-field, high frequency p-EPR

- Increased polarization
- Increased resolution of g-anisotropy
- Less motional averaging in liquid samples
- Can study samples with large "zero-field splitting"

Toward high frequency pulsed EPR

- High frequency pulsed EPR is an emerging technique.
  - limited by electromagnetic source

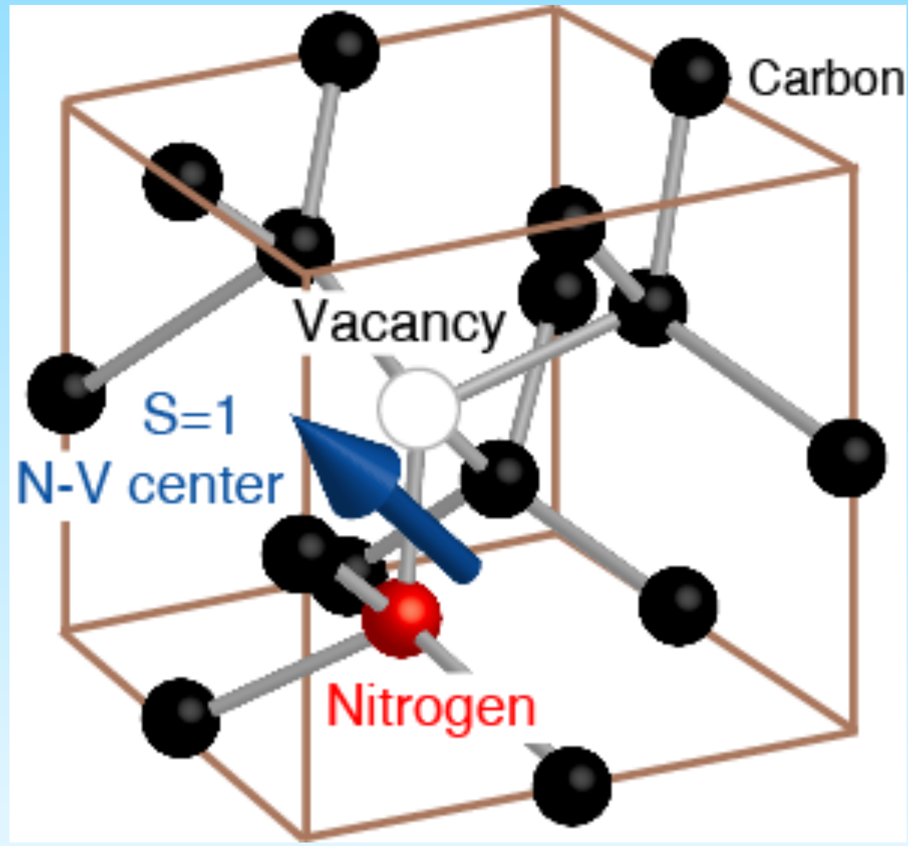


PRL 101, 047601 (2008) PHYSICAL REVIEW LETTERS week ending 25 JULY 2008

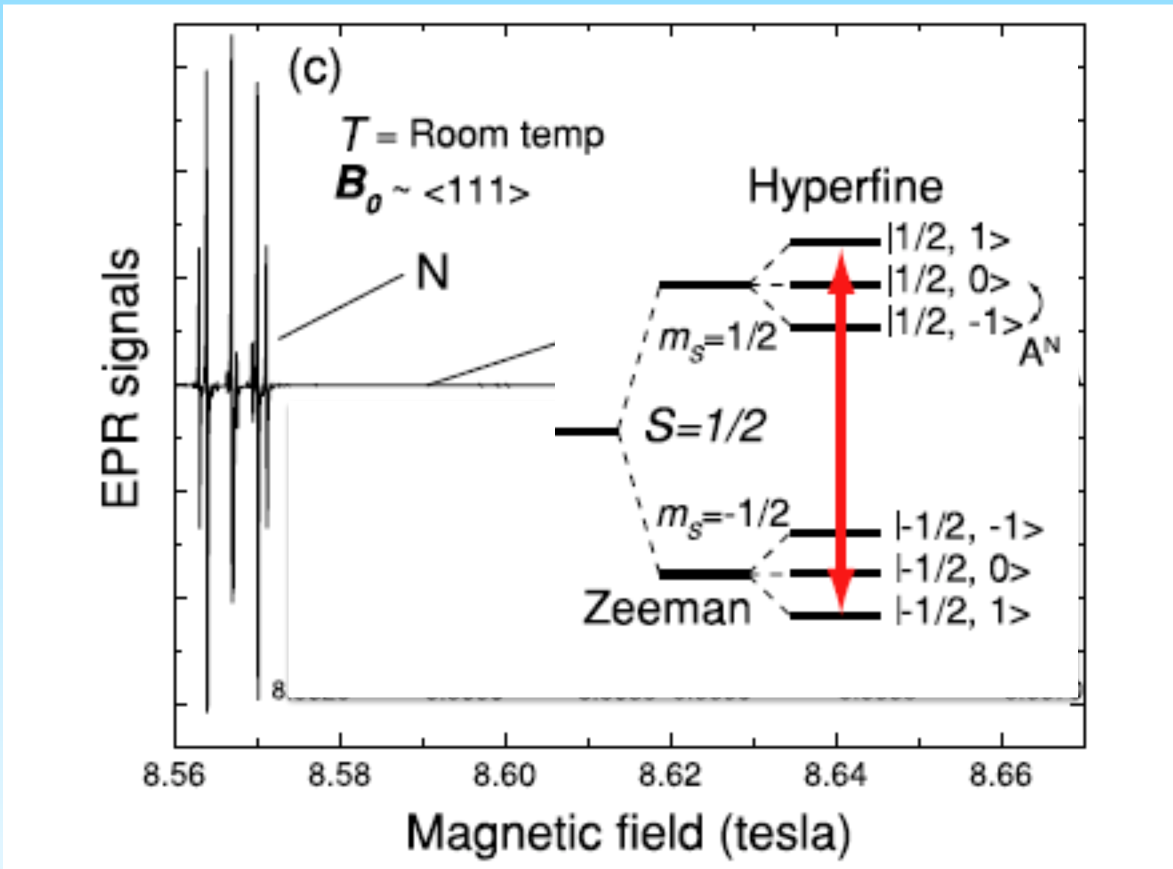
Quenching Spin Decoherence in Diamond through Spin Bath Polarization

Susumu Takahashi,[1,*] Ronald Hanson,[2,3] Johan van Tol,[4] Mark S. Sherwin,[1] and David D. Awschalom[3]

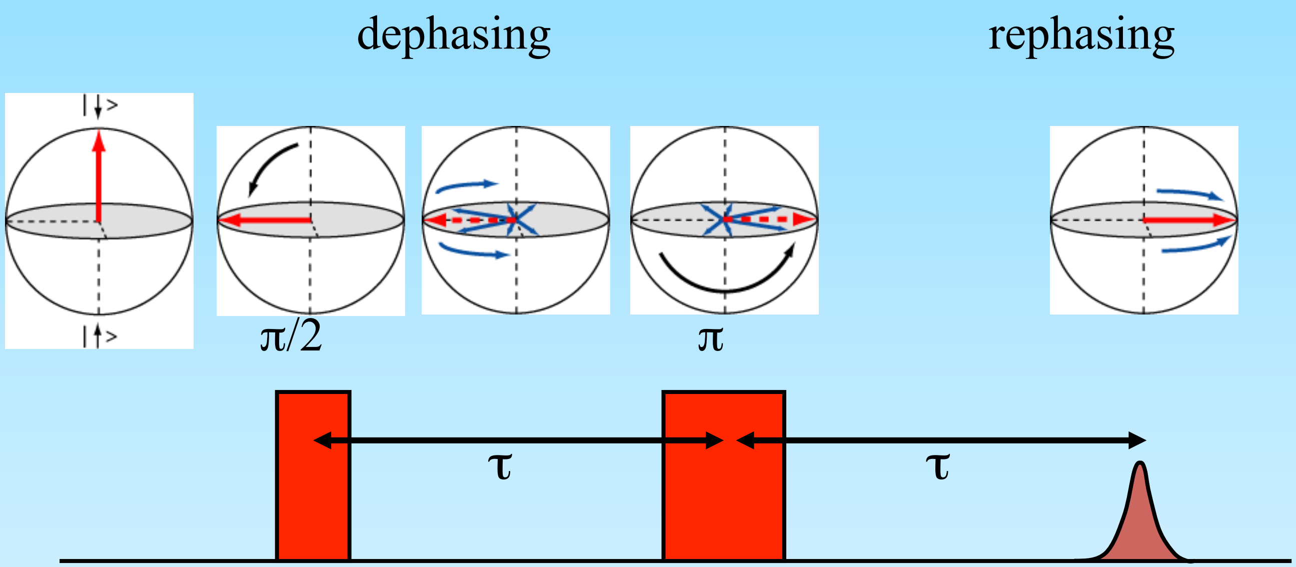
Nitrogen and N-V centers in diamond



240 GHz EPR of N in diamond



Spin echo measurements

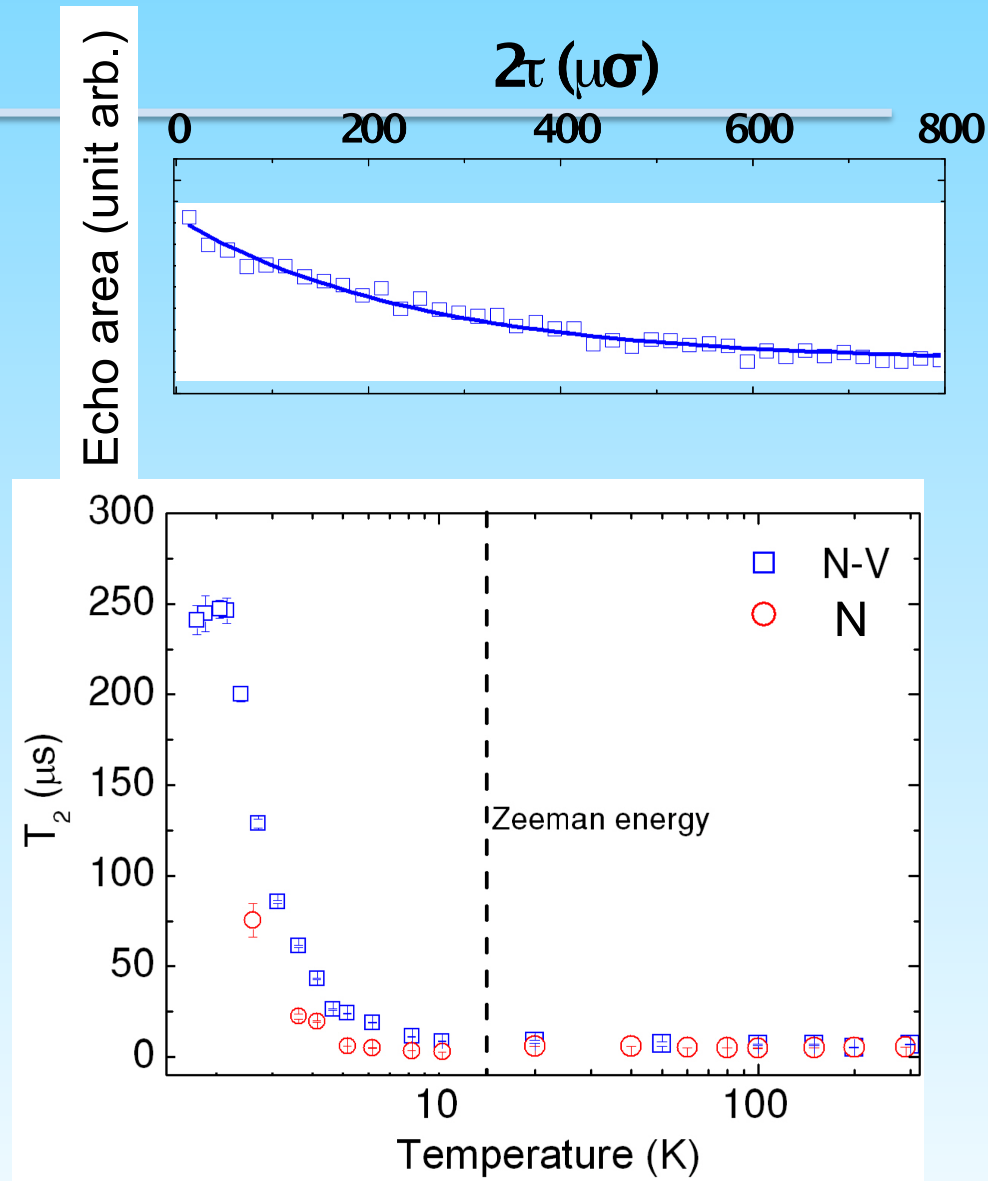


- T_2 obtained by exponential fit to echo strength
- For 30 mW, π/2 pulse 500 ns typical for s=1/2 (no cavity)

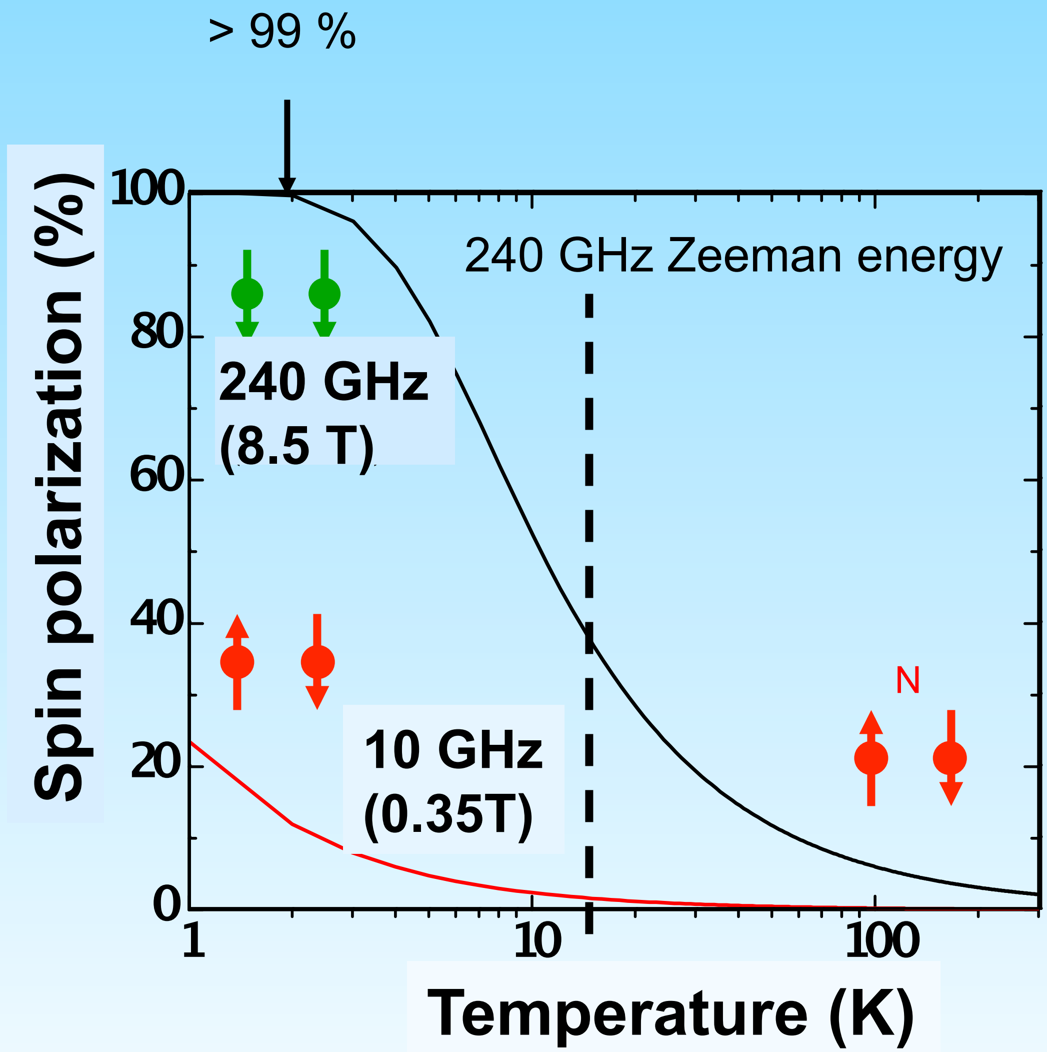
T-dependence of decoherence in diamond

N-V:

- T>11.5 K
  - $T_2 = 6.7\ \mu s \rightarrow 8.3\ \mu s$
- T < 2 K
  - $T_2 \sim 250\ \mu s$

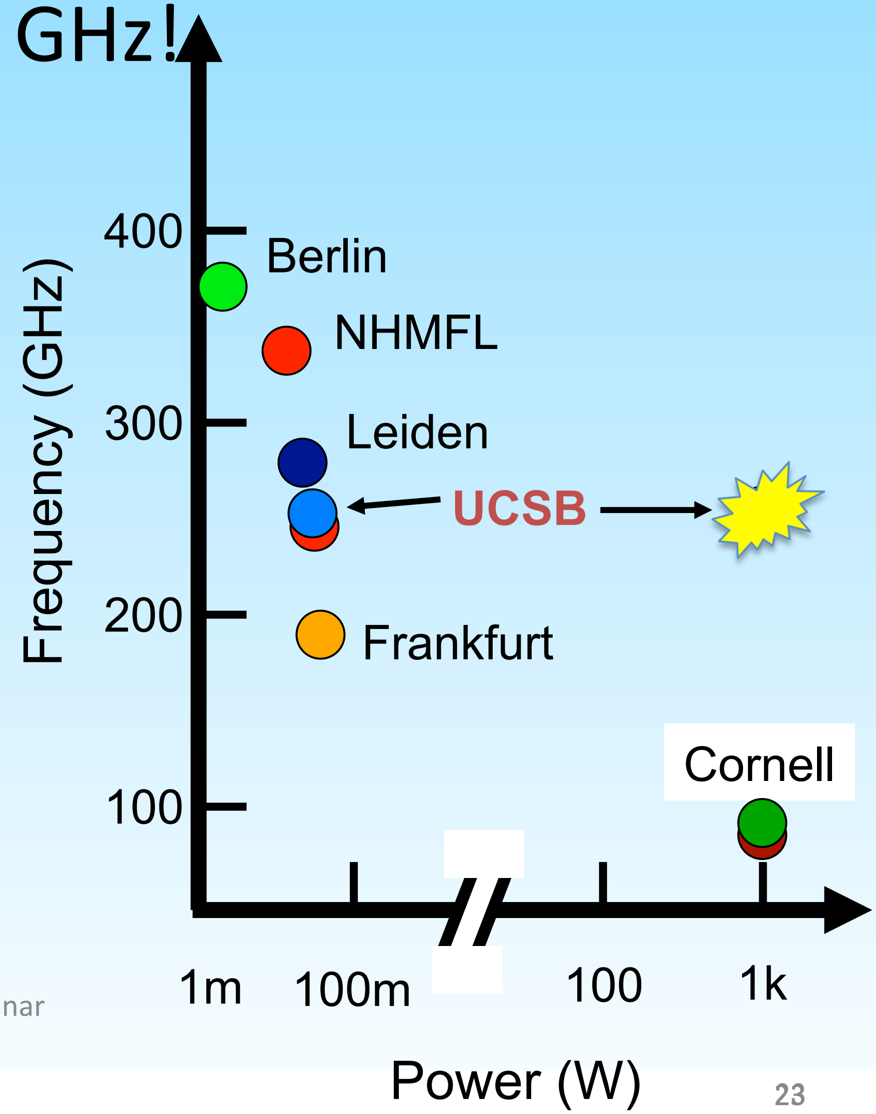


Spin fluctuations quenched at low T and high B



FEL-powered pulsed EPR

- Flip spins in 6 ns @ 240 GHz!
- Come back next week.



Recent and ongoing research

- Pulsed EPR at 0.24 THz
- Frequency-domain vector spectroscopy
  - Water
  - Proteins in solution*
  - Testing detectors
- Nonlinear spectroscopy

Terahertz vector spectroscopy of aqueous solutions

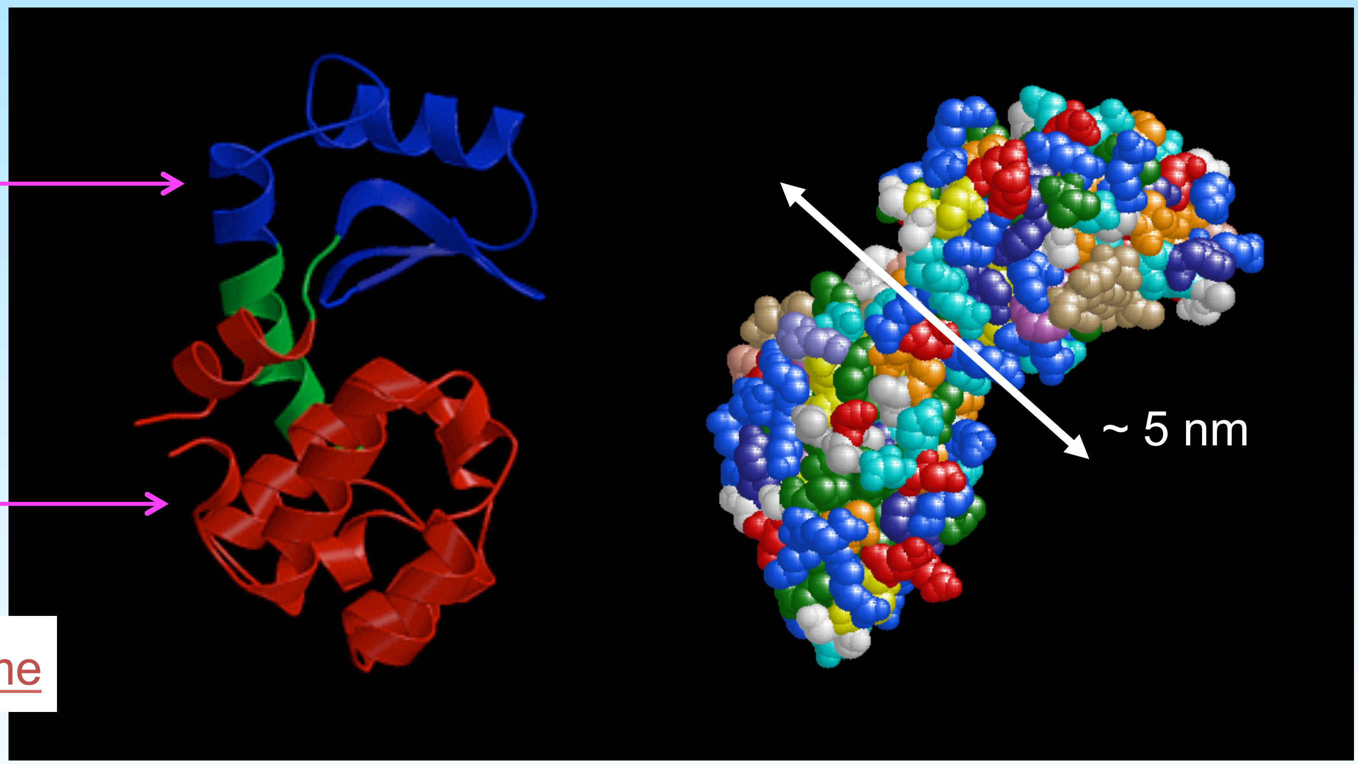
Vinh Nguyen, Jing Xu, Kevin Plaxco, Jim Allen

Motivation

- Water still mysterious
- Protein dynamics in solution
- Chemistry?

Domain 1

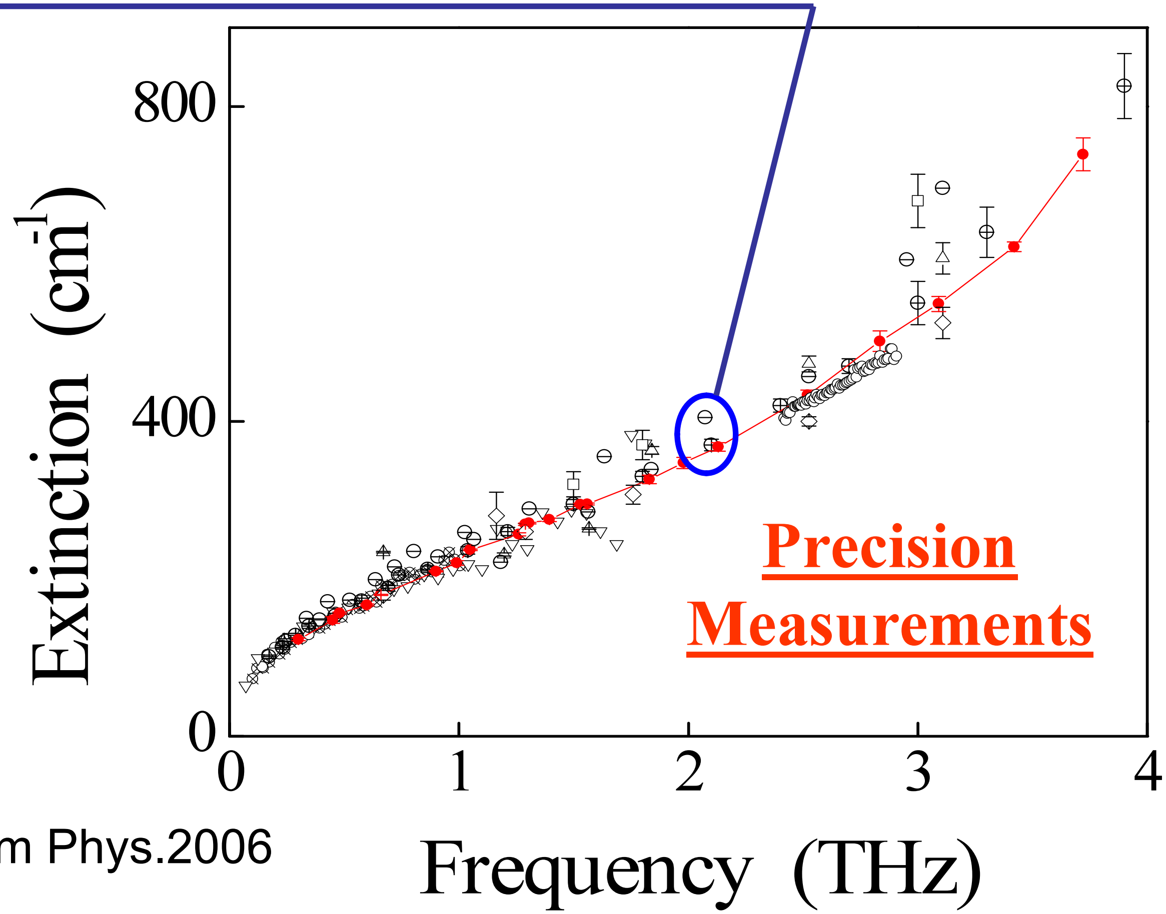
Domain 2



T4 Lysozyme

Challenge: water is ~black!

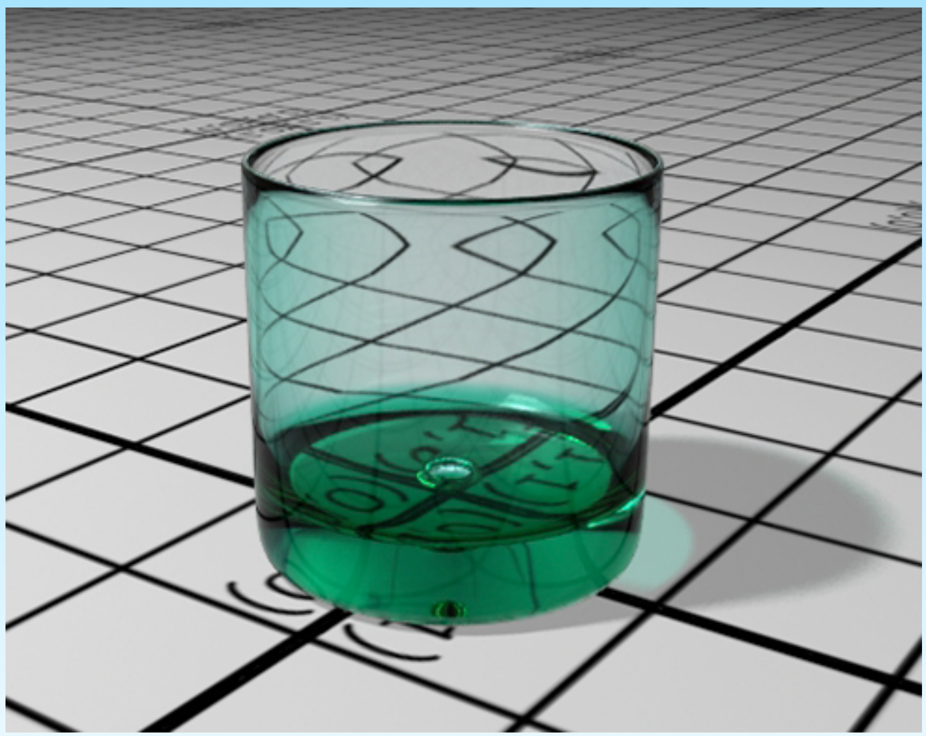
1mm water ~ 10^{18} attenuation



Xu, Plaxco, Allen, J. Chem Phys.2006

Fundamental optical phenomena

- Refraction and absorption



Related fundamental quantities

- Complex dielectric function

$$\tilde{\varepsilon}(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$$

ε_1: α Energy stored per unit volume

ε_2: α Energy dissipated per unit volume

- Complex index of refraction

$$\tilde{n} = \sqrt{\varepsilon_1 + i\varepsilon_2} = n + i\kappa$$

n: refraction

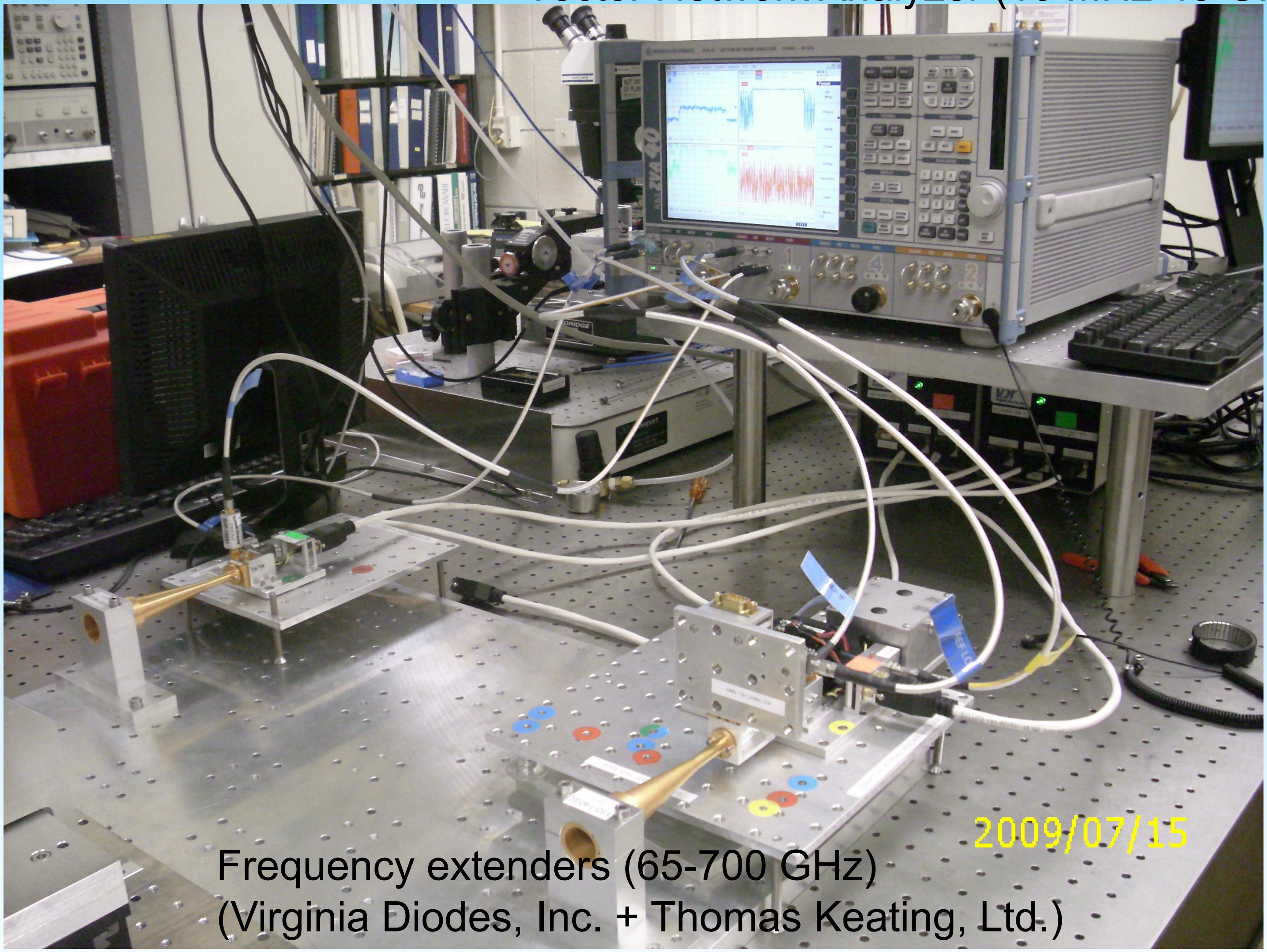
κ: attenuation

What can we learn from $\tilde{\varepsilon}(\omega)$?

- charge dynamics
- charge density
- electronic relaxation times
- Frequencies of classical or quantum oscillations
- . . .
- detailed comparison with microscopic theory

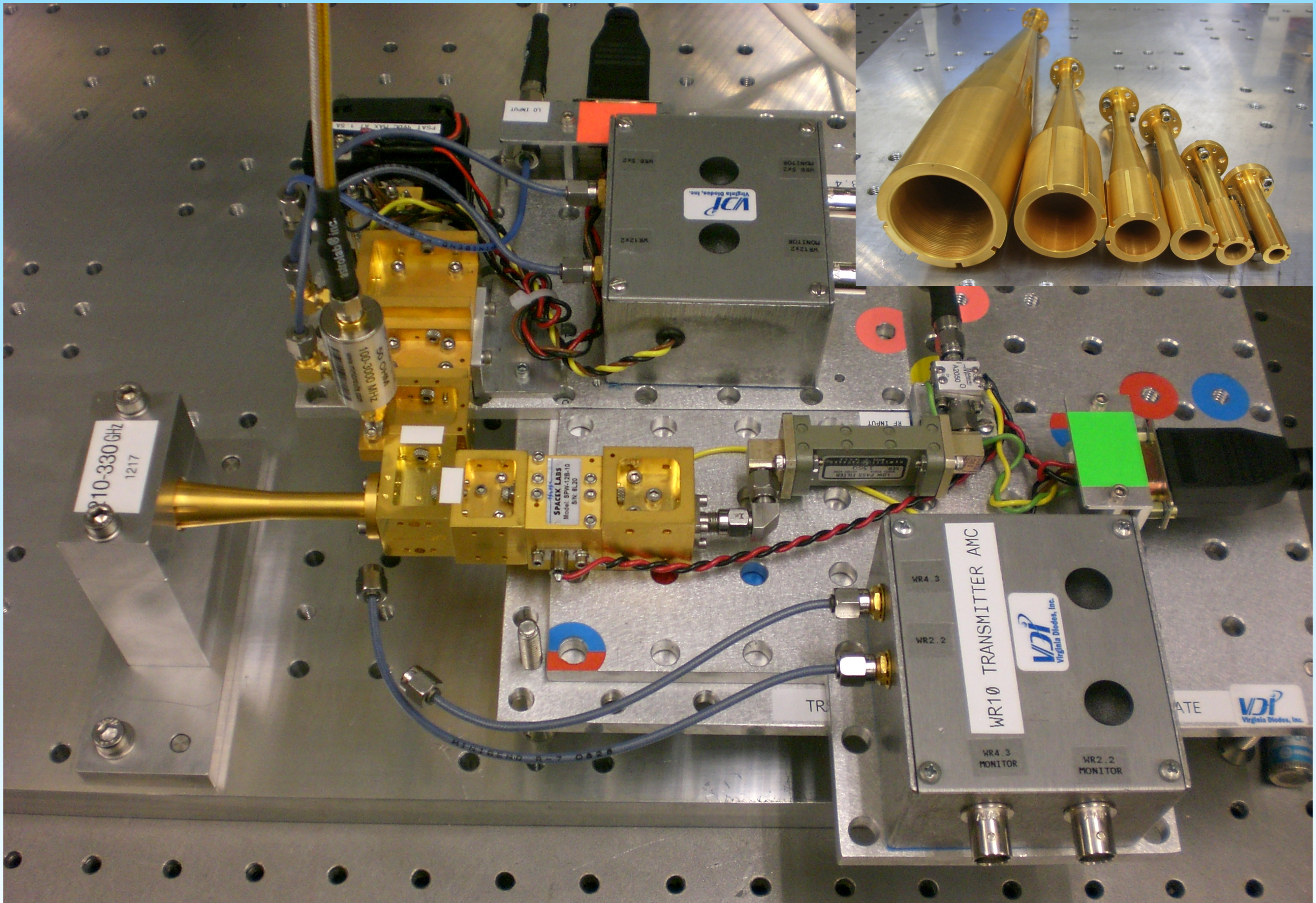
UCSB 65-700 GHz vector spectroscopy system

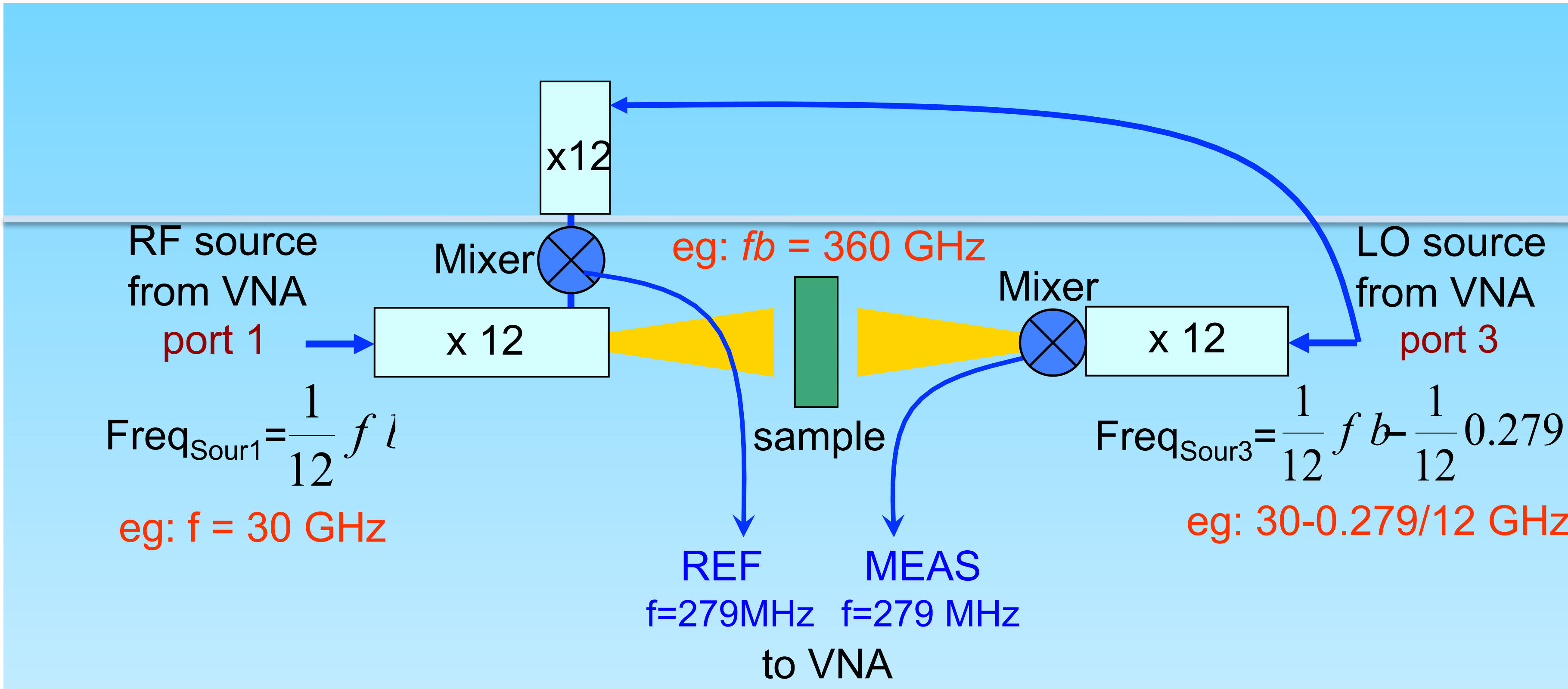
Vector Network Analyzer (10 MHz-43 GHz)



Frequency extenders (65-700 GHz)
(Virginia Diodes, Inc. + Thomas Keating, Ltd.)

Frequency multipliers+ mixers+ horns

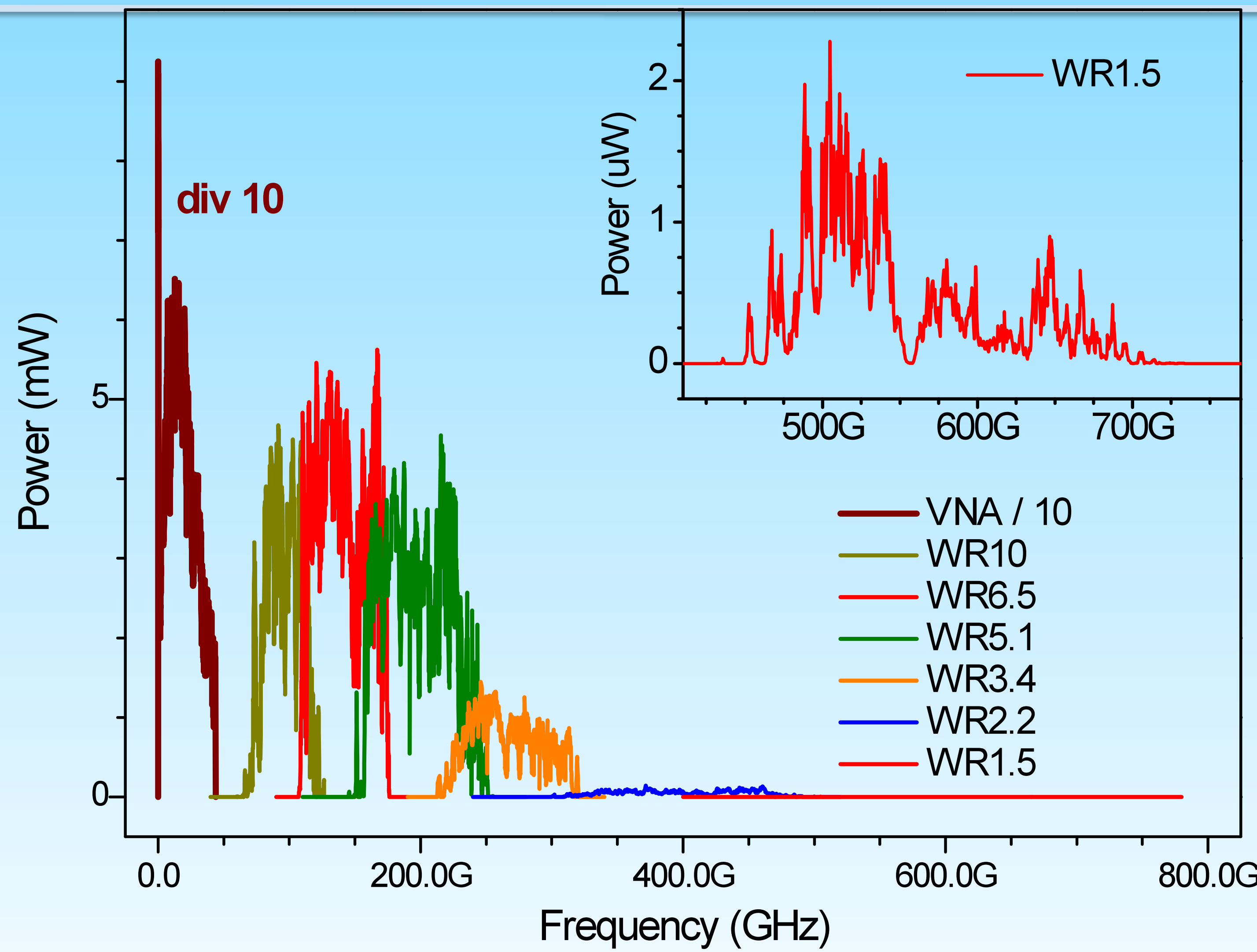




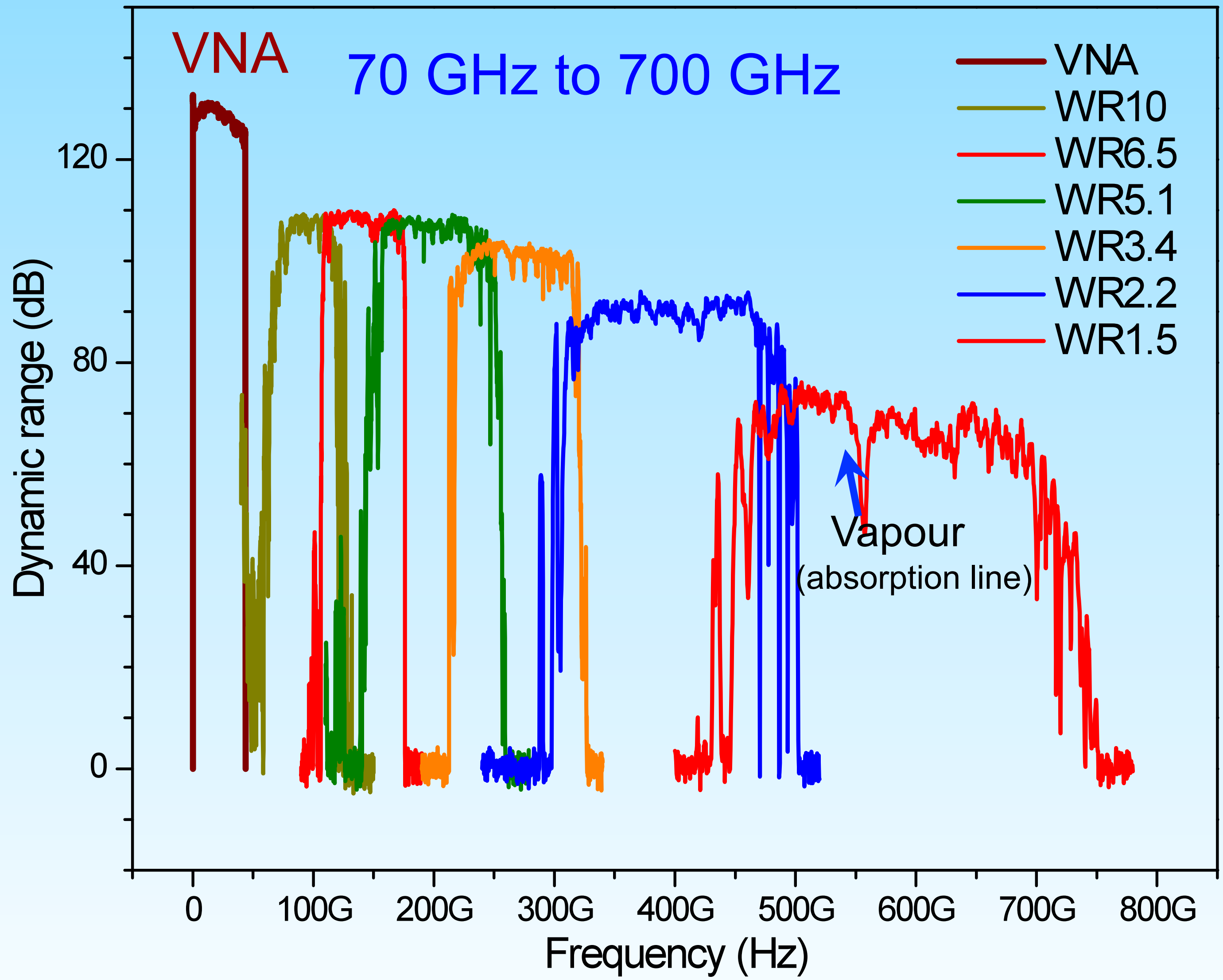
Frequency extension

No.	Freq. band	Freq. Range (GHz)	Freq. factor	Horn dia. (mm)	Length (mm)
#1	WR10	75 – 110	x 3	40	234.12
#2	WR6.5	110 – 140	x 4	28	139.50
#3	WR5.1	140 – 220	x 6	20	100.80
#4	WR3.4	210 – 330	x 9	15	82.50
#5	WR2.2	280 – 440	x 12	12	54.20
#6	WR1.5	440 – 660	x 18	9	37.70

Spectra – linear scale



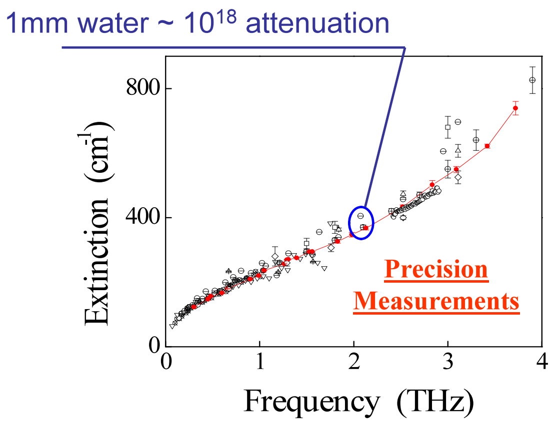
60-110 dB dynamic range!



Measuring sub-THz dielectric properties of aqueous solutions

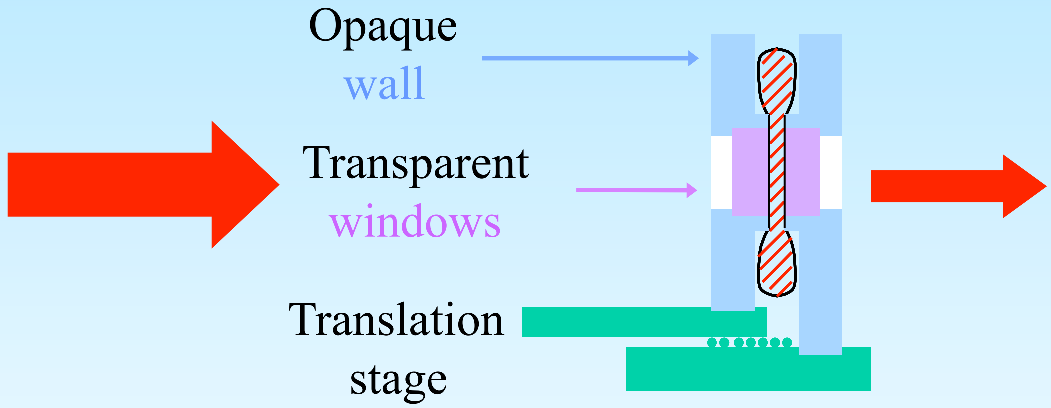
Precise measurement of attenuation and phase shift

Water, water, water



$$I = I_0 e^{\alpha z}$$

$$\Delta A = -\Delta(Ln(I_{transmitted})) \propto \alpha \cdot \Delta l$$

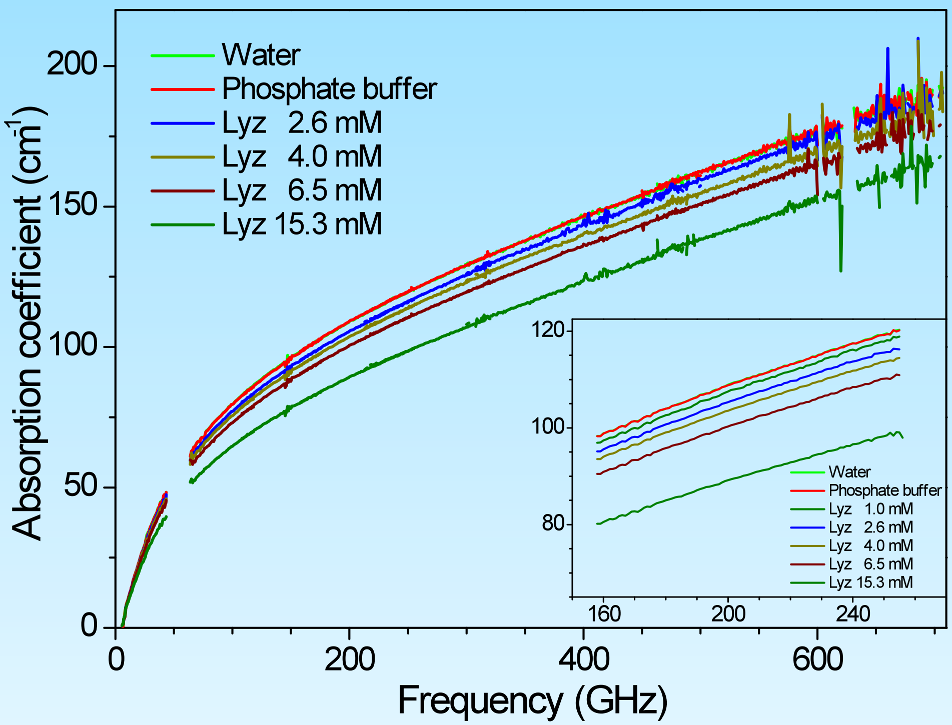


(a)

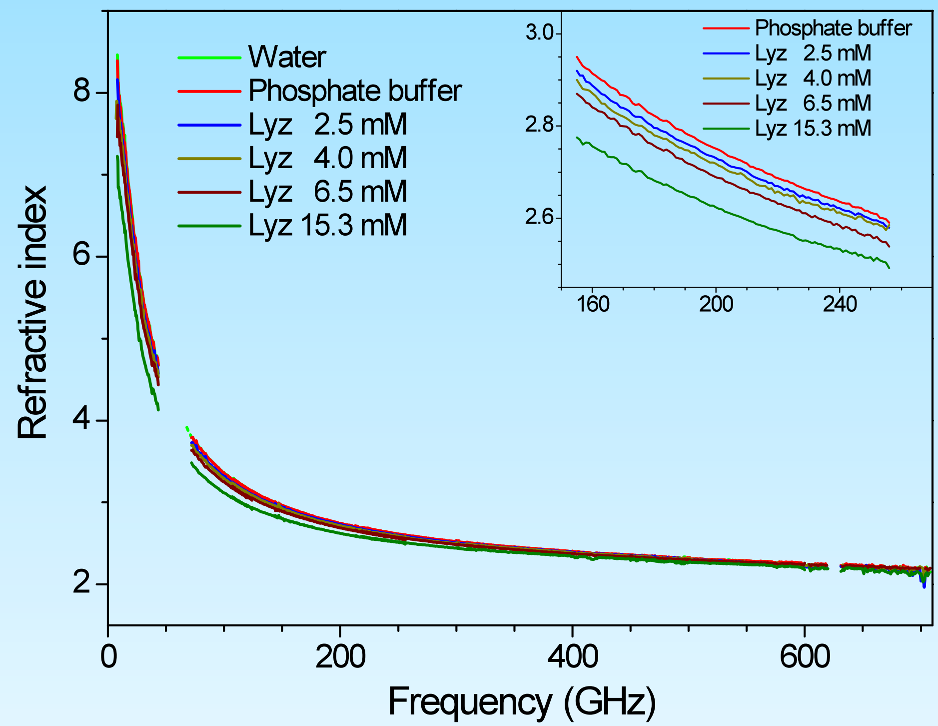
Variable Path Length Sample Cell

Absorption and refraction of aqueous solutions

Absorption coefficient



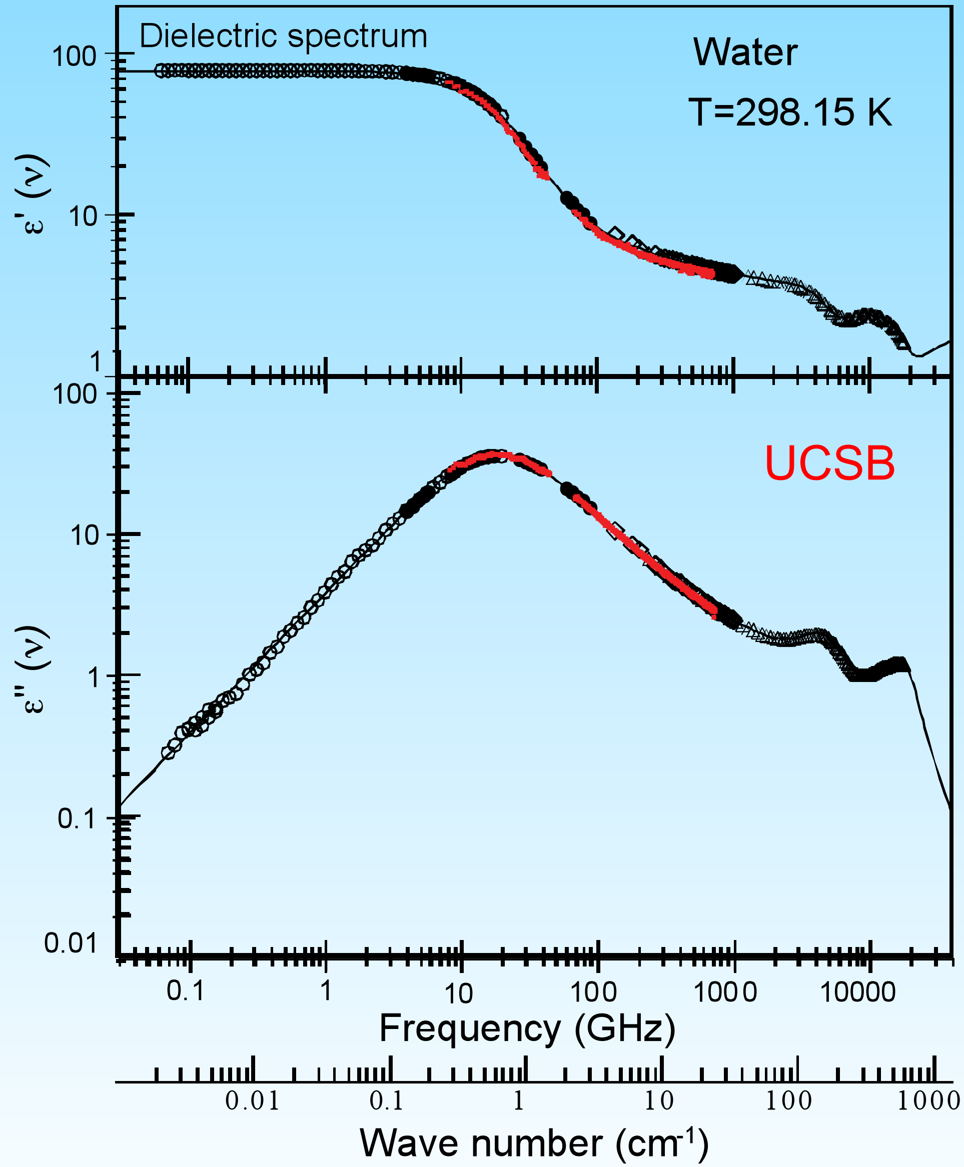
Refractive index - n



$$\Rightarrow \begin{cases} \varepsilon_1 = n^2 - K^2 \\ \varepsilon_2 = 2nK \end{cases}$$

Complex dielectric constant - water

$$\Rightarrow \begin{cases} \varepsilon'_{wat} = n^2 - K^2 \\ \varepsilon''_{wat} = 2nK \end{cases}$$



Protein hydration and dynamics

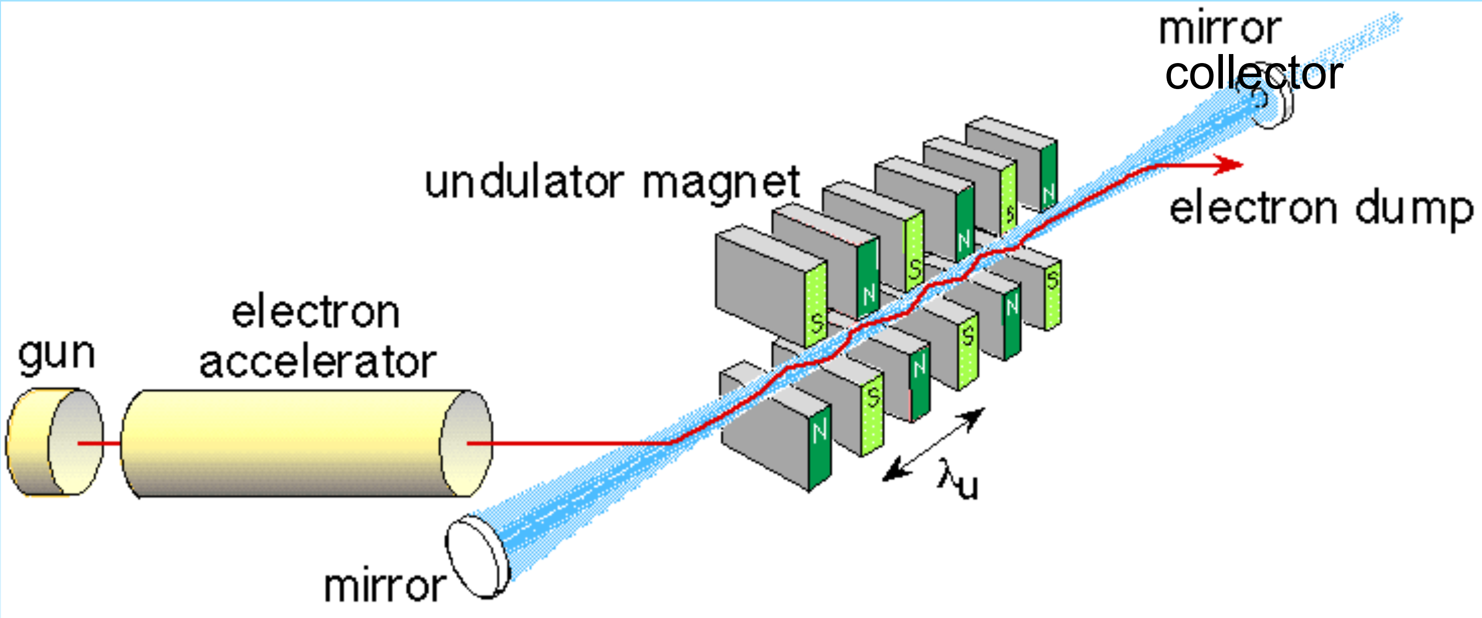
- Come back in 3 weeks:
- **Oct. 28:** “Probing the dynamics of biomolecules in liquid water,” by Dr. Vinh Nguyen, ITST.

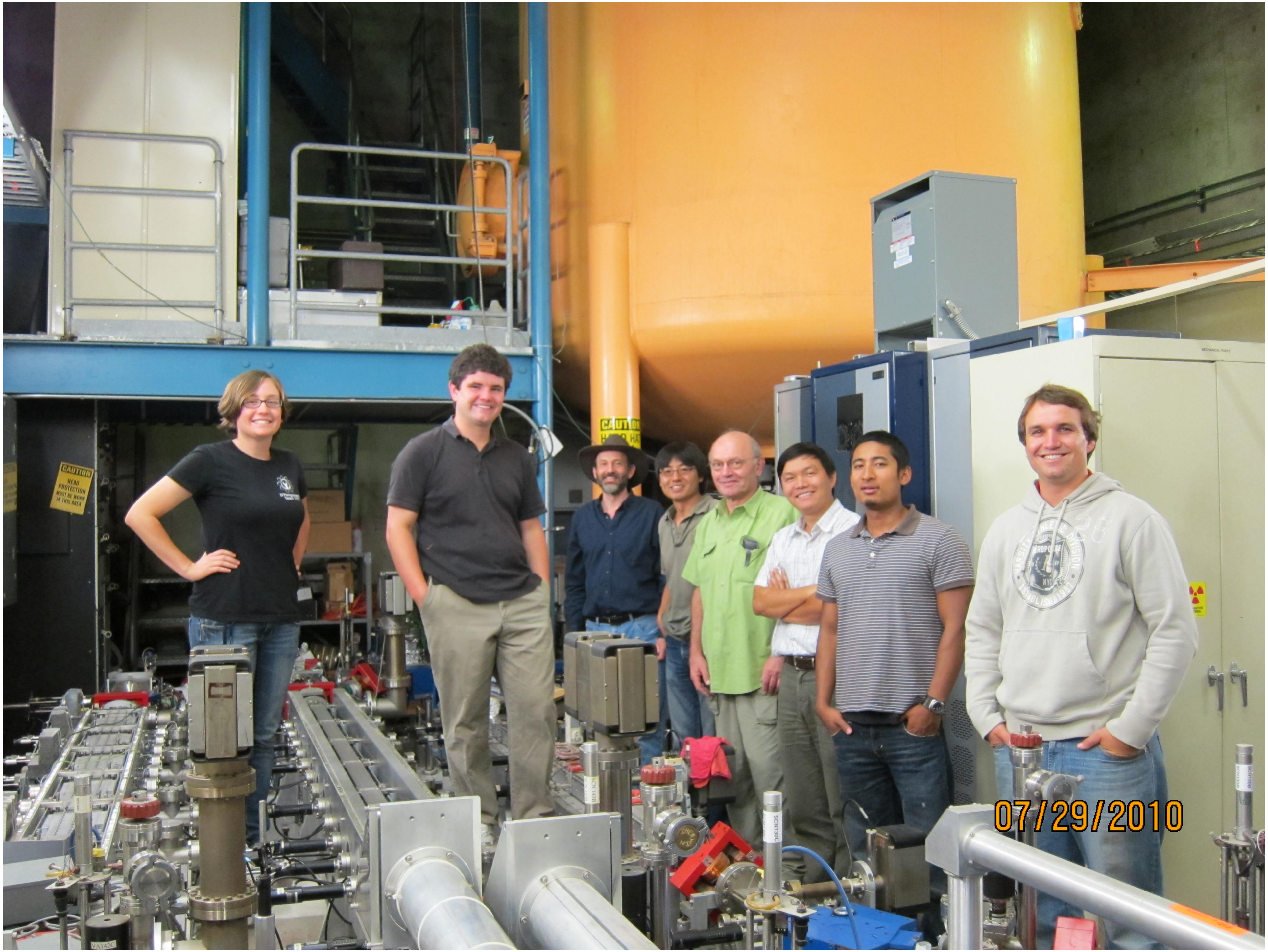
Nonlinear spectroscopy

- Explore THz physics beyond equilibrium!
  - Fundamental physics
  - Devices
  - Life!
- Use UCSB Free Electron Lasers
  - ~0.1-5 THz
  - ~1 kW peak power
  - **Highest peak brightness in the world for tunable THz source.**

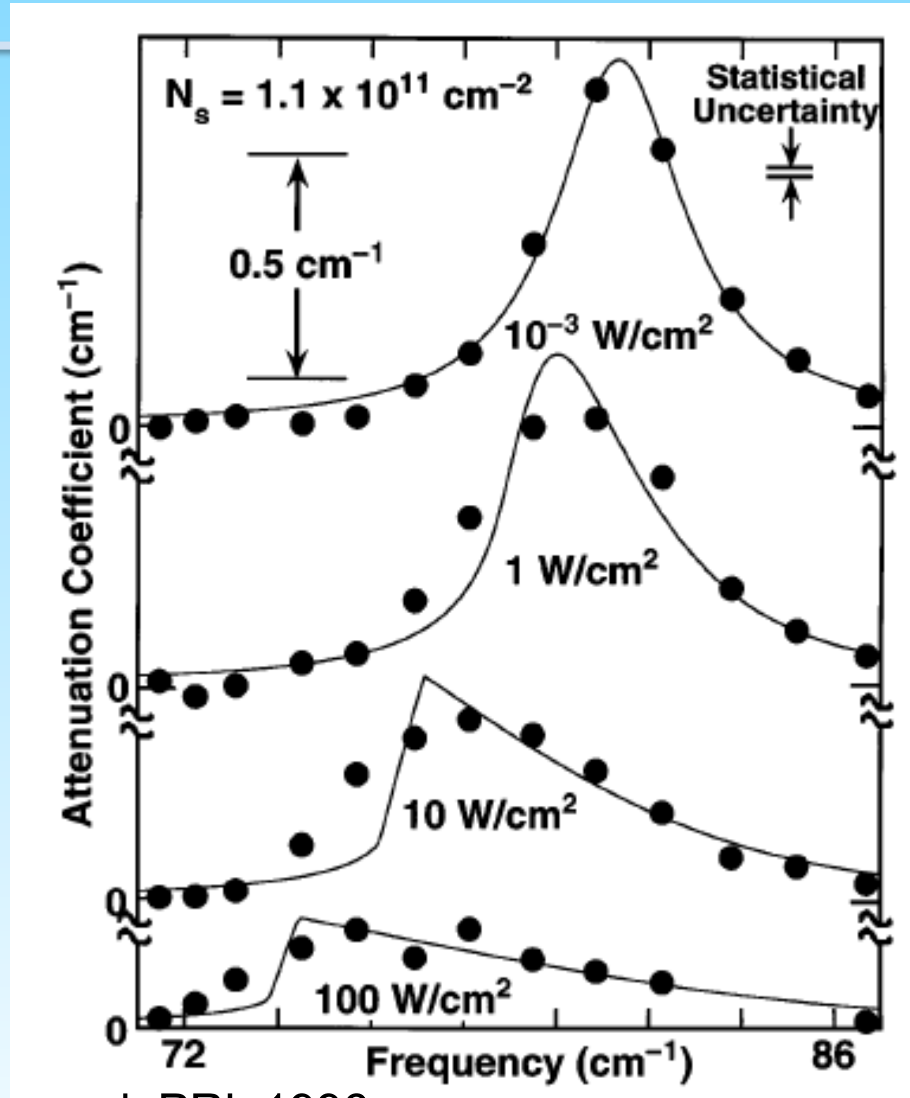

UCSB
Institute for
Terahertz
Science and
Technology
UCSB
Free-
Electron
Lasers
Free-Electron Laser User's Labs

Free-Electron Lasers



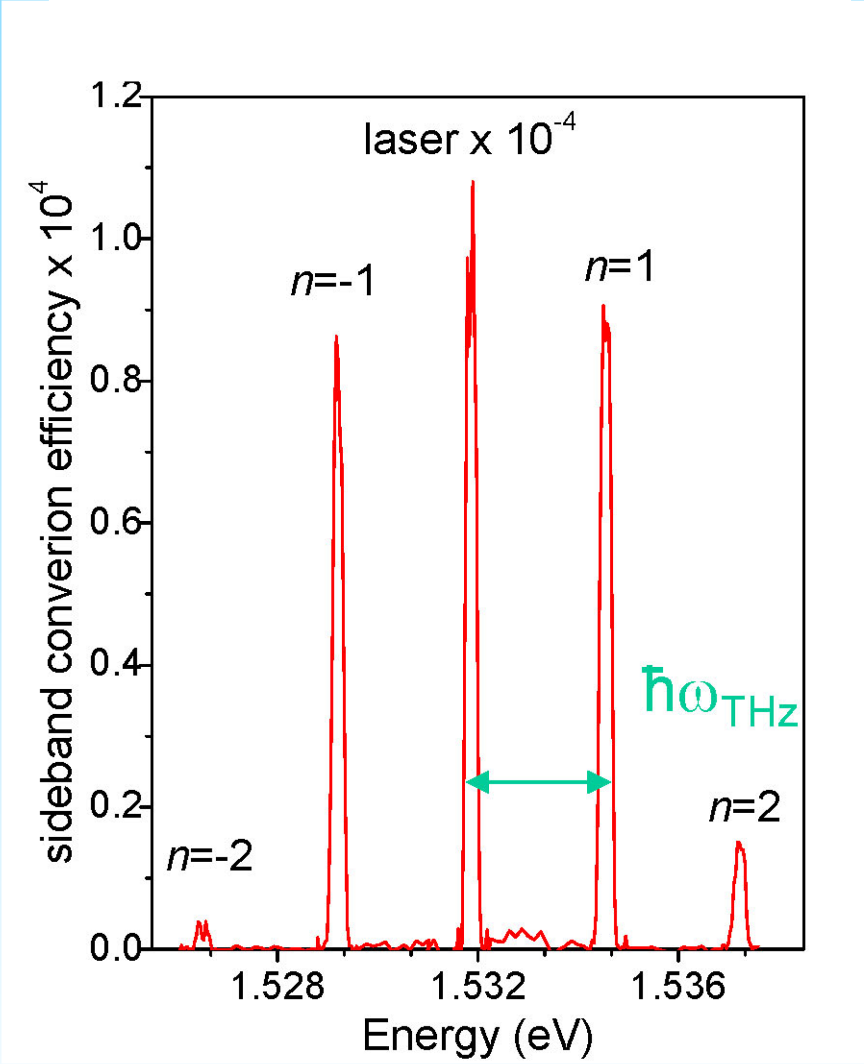

CAUTION
HEAD
PROTECTION
MUST BE WORN
IN THIS AREA
07/29/2010

Nonlinear absorption



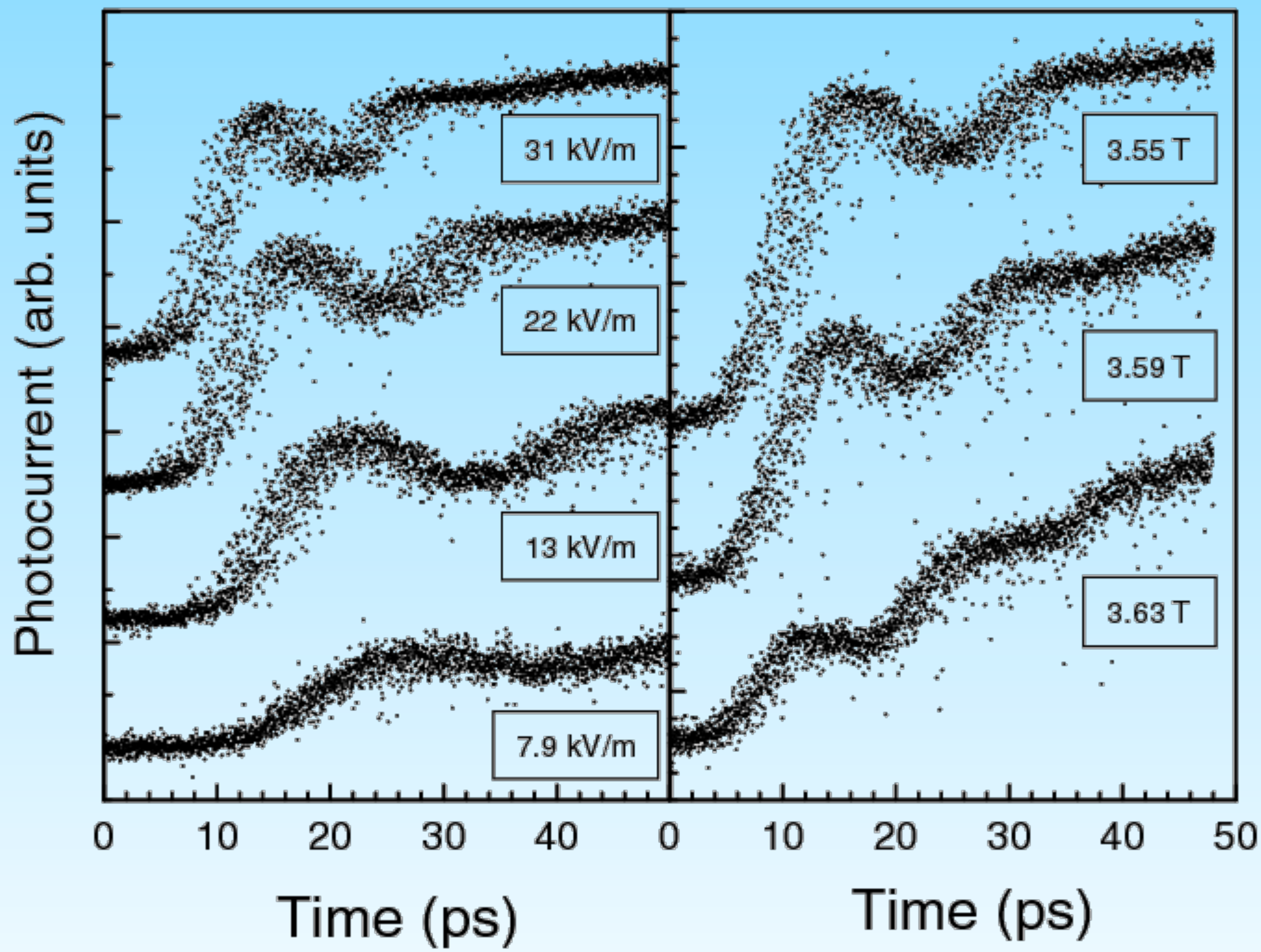
Craig, Galdrikian, Heyman, Markelz,
Williams, MSS, Campman, Hopkins, Gossard, PRL 1996

Terahertz sidebands on optical carrier



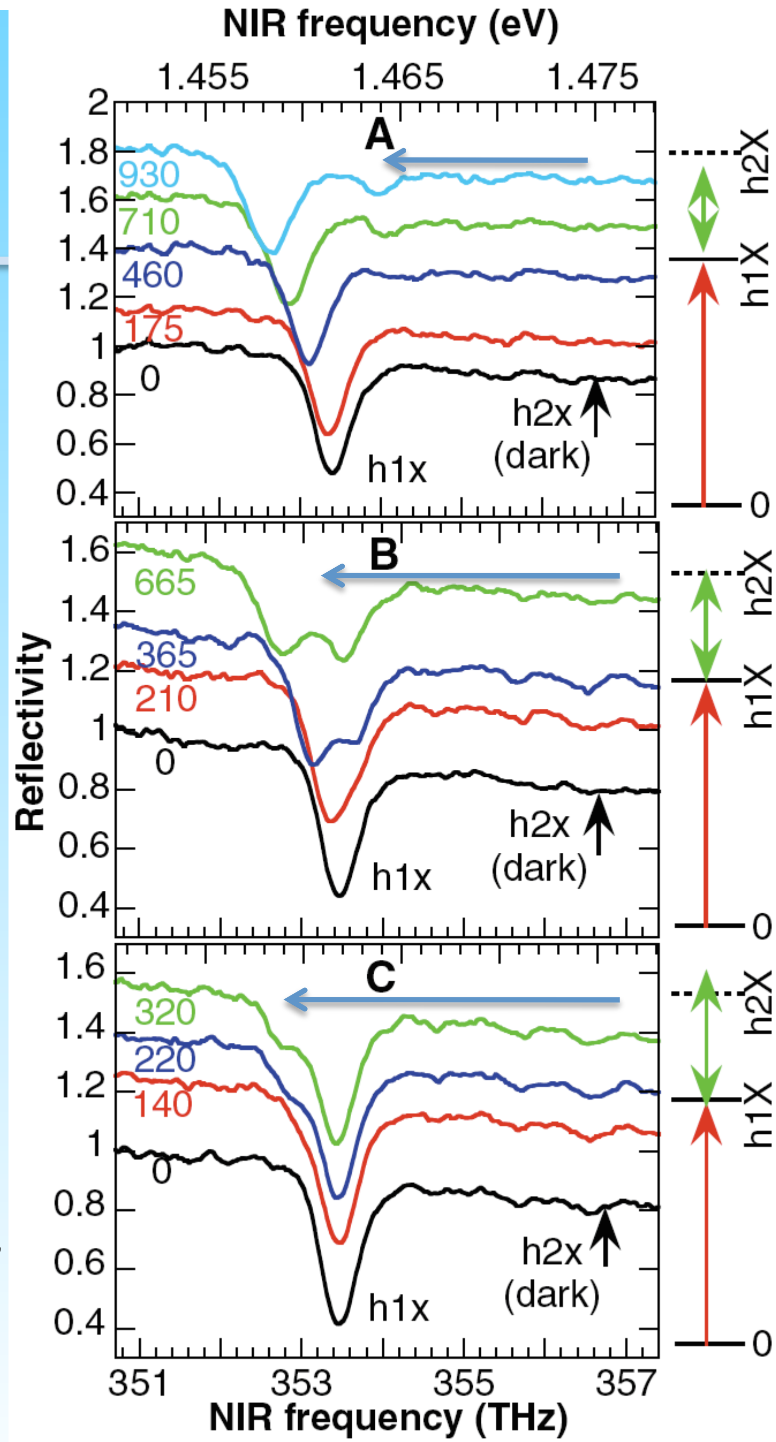
Ciulin, Carter, MSS, Huntington, Coldren, PRB 2004

Rabi oscillations of impurity-bound electrons



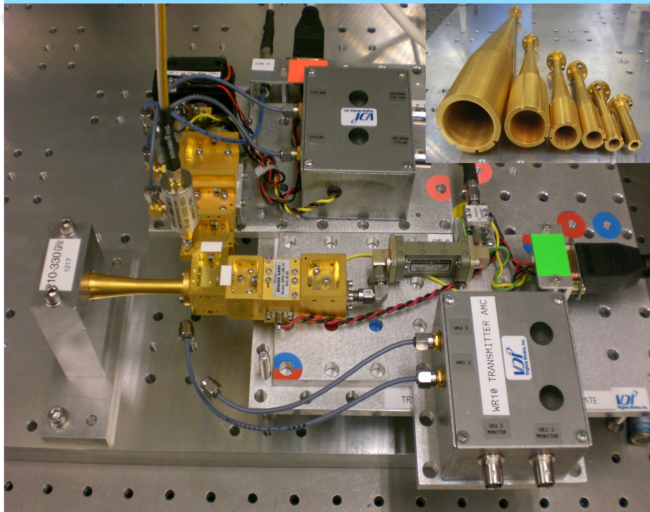
Cole, Williams, King, MSS, & Stanley, Nature, 2001

Changing band structure of quantum well

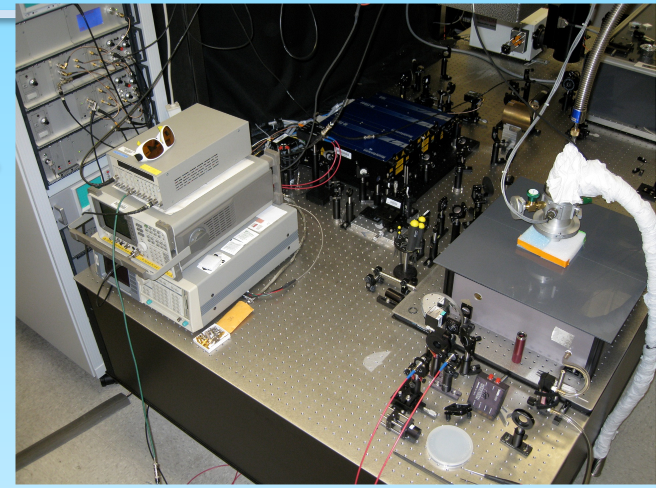


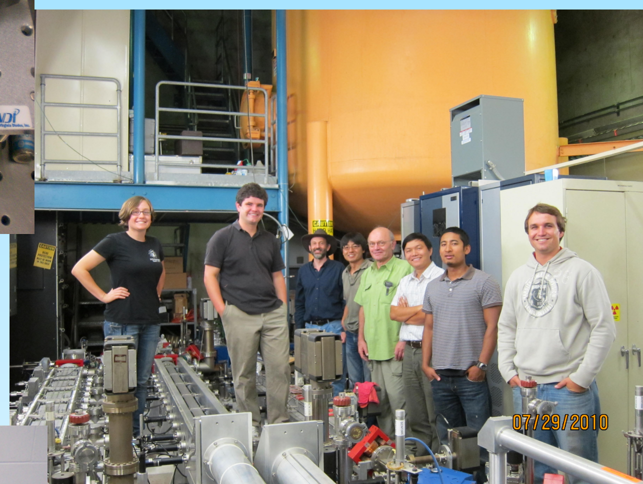
Carter, Birkedal, Wang, Coldren, Maslov, Citrin, MSS, Science, 2005

ITST THz sources and systems



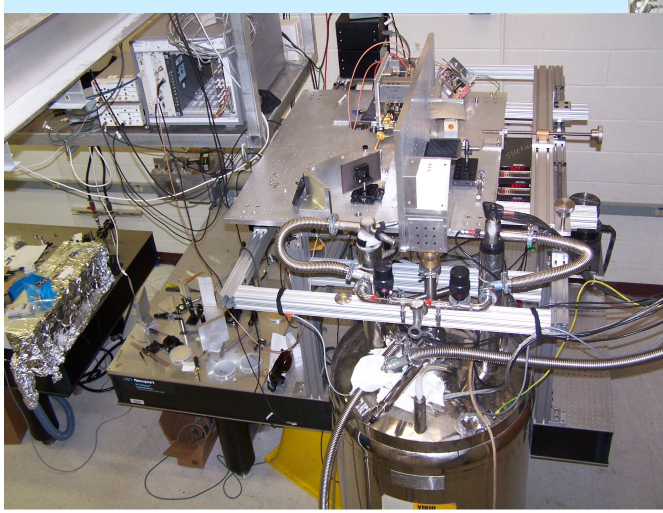
Video-rate time-domain
vector spectrometer
0.3-3 THz





Frequency-domain
vector spectrometer
0.07-0.7 THz

FTIR spectrometer
~1-100 THz



UCSB FELs
0.1-4.8 THz, kW power

cw and pulsed EPR
0.24 THz

Acknowledgements

- Present Sherwin group:
  - Chris Morris, Ben Zaks, Devin Edwards, Vinh Nguyen, Sascha Preu, Wendy Xu, Louis-Claude Brunel
- Alumni:
  - Susumu Takahashi, Dominik Stehr, . . .
- Songi Han, Jim Allen, Kevin Plaxco, Art Gossard, Pierre Petroff . . .