Lecture Notes Chem 524 – IR spectra (Part 16)- 2013

For HTML of 2005 notes, click here

XII. Infrared Spectroscopy — focus on vibrational transitions (Read Chap 14)

A. Regions: -- near IR (800-2500 nm — quartz optics/W-I lamp, diode or thermal detect)

anharmonic vib, overtone and combination bands. Return to this later, specific use

-- mid IR (2500-25000 nm, 2.5-25μ, 4000-400 cm^{-1}) – (lower limit arb., due to KBr b/s in FTIR)

(glowers, MCT or TGS detect, FTIR best for routine spectra, optics spec. salts-materials)

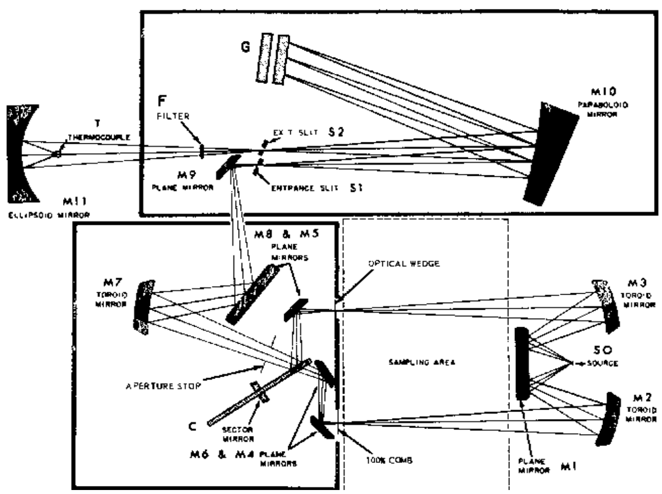
Access fundamental vibrations, qual. anal. via fingerprint pattern in vibrational modes.

-- far IR (25μ → ? , 400 cm^{-1} → ?)

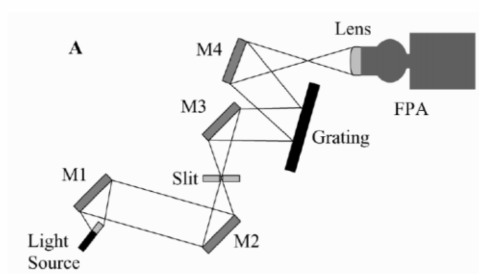
(difficult: source, detector, S/N) access torsions, lattice vibration, large amplitude mode

new approach uses THz lasers, excite diode with fs laser, re-emit pulse – FT for spectra

B. Dispersive IR (still around, rarely made new – unless homemade from components) – exception ↓



New Developments in Planar Array Infrared Spectroscop
I. Pelletier, C. Pellerin, D. Bruce Chase, John F. Rabolt
APPLIED SPECTROSCOPY **59**, **156**, 2005



This approach opens up new ways to get either spatial or time dependent information

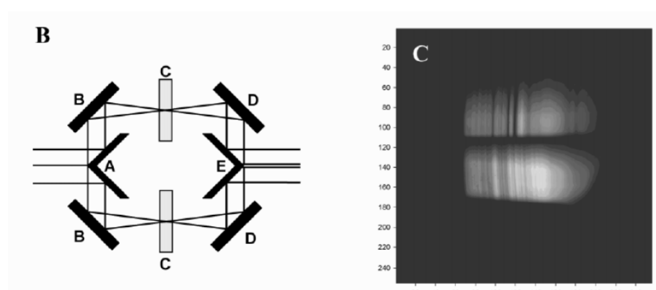
Dispersive revival

-- same principle as uv/vis double beam
-- chop between ref and sample, meas. Difference
--sample sees source direct

--same idea as diode array uv-vis spectrom.
--detector 2-D can do ref and sample simult.
by putting one above other, sum separate

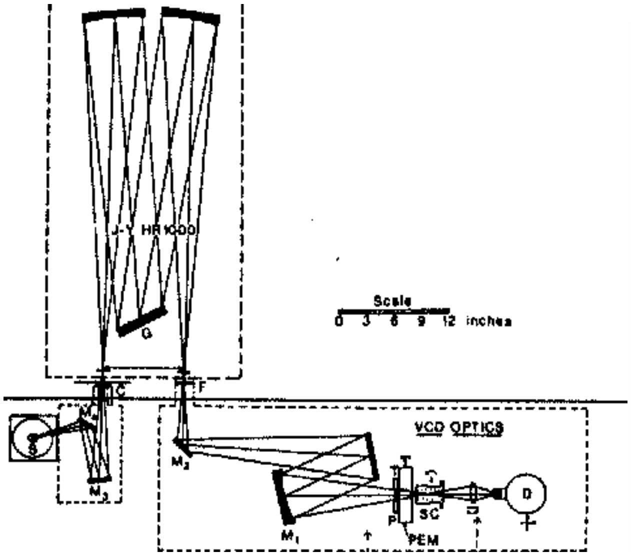
-- multiple gratings/filters to cover range
- scale sometimes change, near to mid-IR

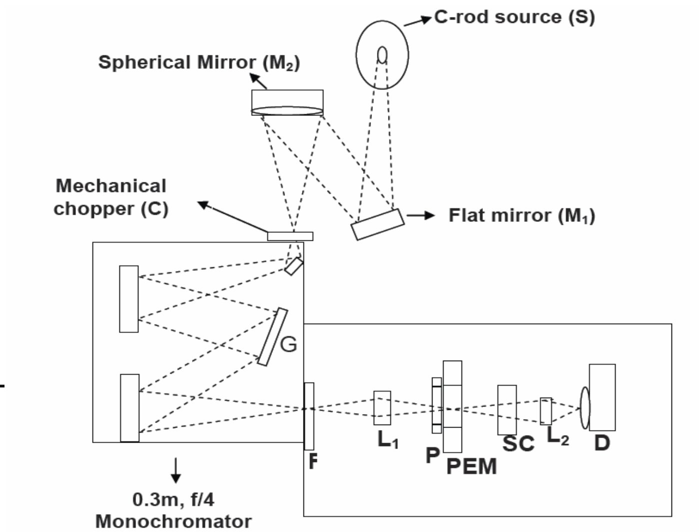
-- I/I_0 determined by varying transmission in
reference beam with a variable attenuator
often a comb or wedge translate at slit
coupled to readout, chart recorder



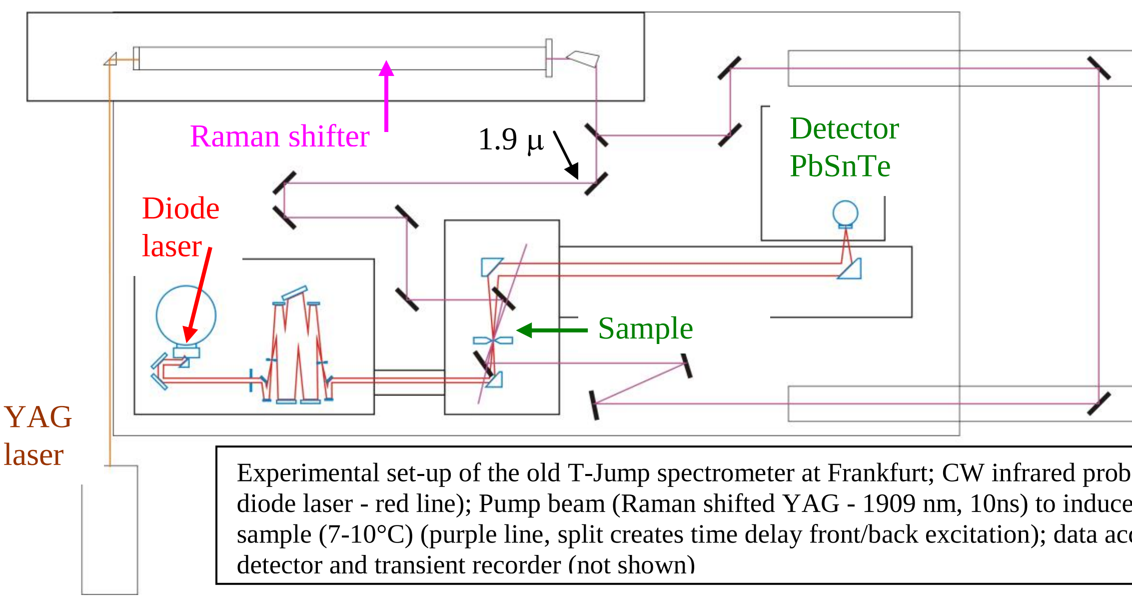
IG. 1. (**A**) Scheme of the PA-IR spectrograph. (**B**) Scheme of the dual-beam accessory. (**C**) Spectral image recorded with a polystyren
laced in the top portion of this accessory and air in the bottom portion. On this image, bright areas represent high single beam intensity re

-- homemade for special purposes (TAK group) - modulation or kinetics measurement, single beam





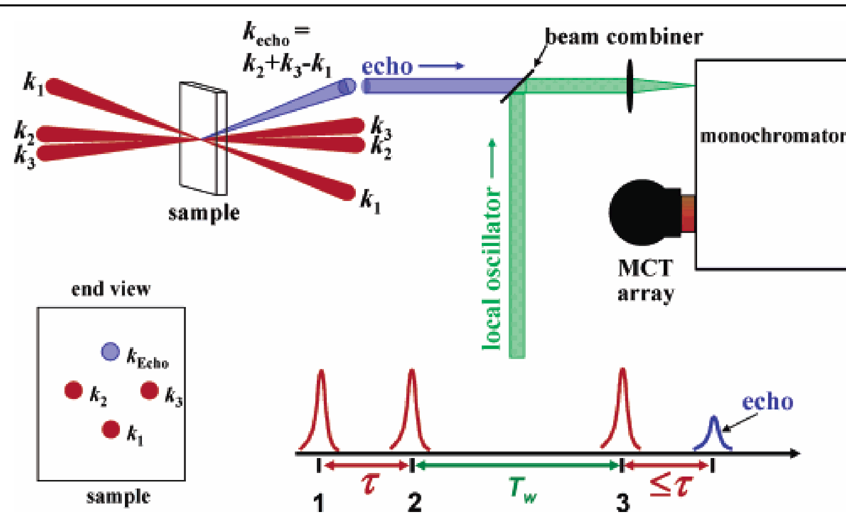
-- also laser based spectrometers use dispersive element for mode separation



T-jump spectrometer at Frankfurt used monochromator to sort modes in diode laser for probing specific IR bands

Experimental set-up of the old T-Jump spectrometer at Frankfurt; CW infrared probe beam (tunable diode laser - red line); Pump beam (Raman shifted YAG - 1909 nm, 10ns) to induce a T-Jump in the sample (7-10°C) (purple line, split creates time delay front/back excitation); data acquisition by MCT detector and transient recorder (not shown)

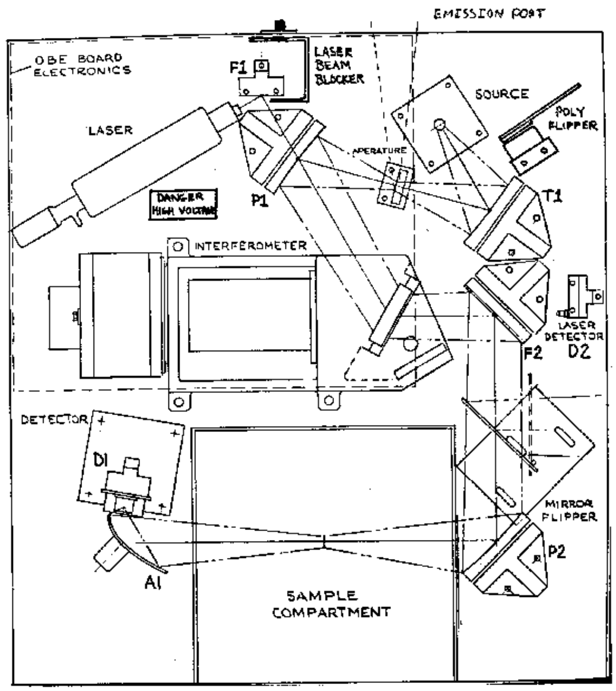
FIGURE 1. Schematic of the ultrafast 2D vibrational echo spectrometer showing the wave vectors (k_i) and the vibrational echo pulse sequence. These use dispersive IR with multi-detector array (MCT) to get spectrum



C. **Fourier Transform** — FTIR dominate usage now and commercial market, single beam) - ***REVIEW***

-- **High end** — air bearing for moving mirror, cooled SiC source, multiple detector (TGS, MCT), high resolution <1 cm^{-1} → 0.001 cm^{-1} (rare), multiple beam splitter, purged

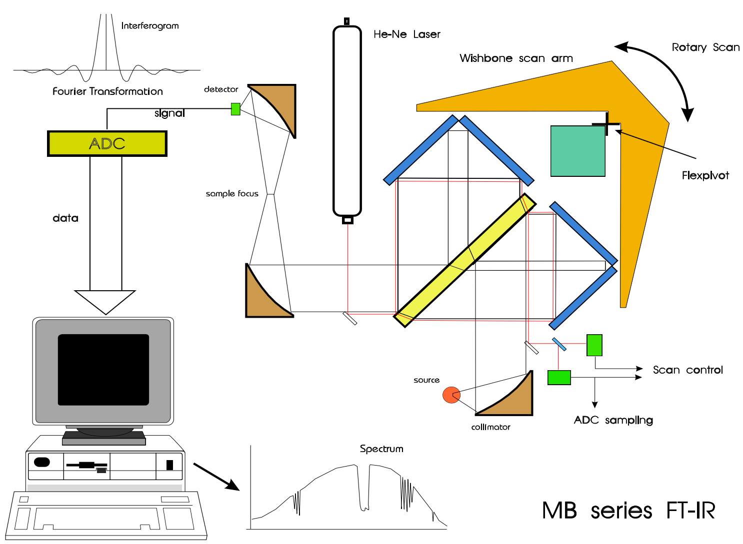
--(old design used white light fiducial mark, current methods count laser fringes)



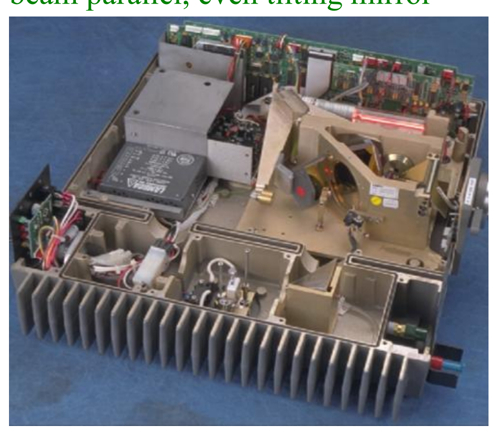
--external bench—used for emission/ Raman/ reflection/ modulation / etc.

-- computer control enables multiple tasks (vary mirror scan speed, number scans, averaging, data processing, deconvolution, subtraction, searches)

--**Low end** — mechanical bearing, corner cube mirrors, restricted speed and lower resolution, >1 cm^{-1}, uncooled source (lower T), unpurged (dessicant), software--more limited processing/automated



Bomem design, corner cubes keep beam parallel, even tilting mirror



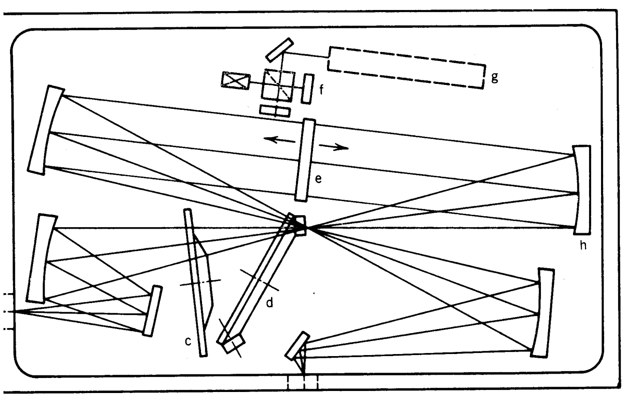
Research level FTIR instruments, all work very well (some examples, also Jasco, Thermo-Nocolet):

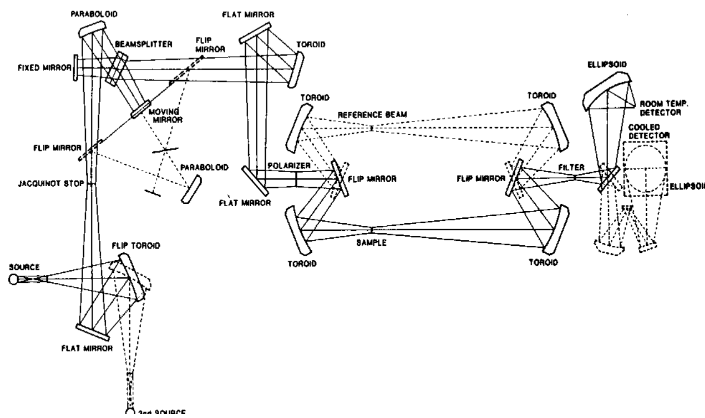



Varian (ne. Digilab) 660   Bruker Tensor,   Vertex   High Resolution   Thermo-Nicolet iS-50R

Typically have multiple ports, dual or more sources and detectors, many sampling options

- **unusual designs** — swing, PE 1700 (pivot), Genzel, 1800 (double B/S), Bomem DA (vertical drop), Bomem Michelson (pivot), sliding wedge – Review of previous interferometer section





RECALL:. mini spectrometers now a big market issue:





Bruker Alpha, small footprint: 30 x 22 cm, Thermo (Nicolet) S-10, showing 2 of variable sample chambers -   JASCO 4000 and Perkin-Elmer 400 similar ideas

BOMEM - bigger yet compact, see notes 7

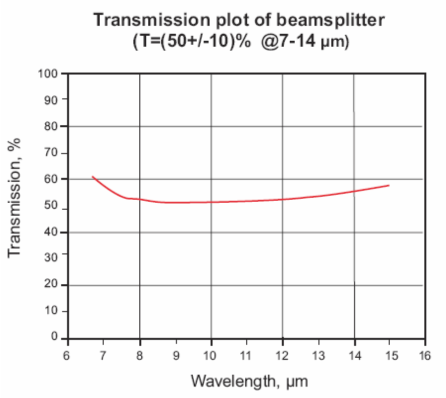
Handheld also available, seen Notes 7 for examples

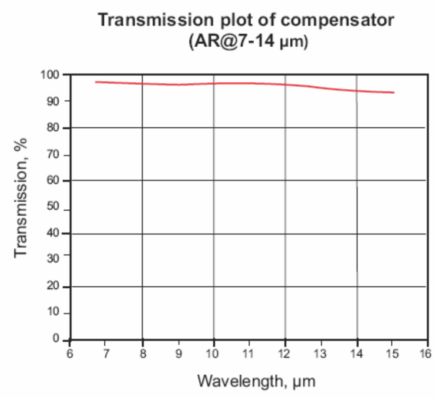
(left) Thermo Ahura

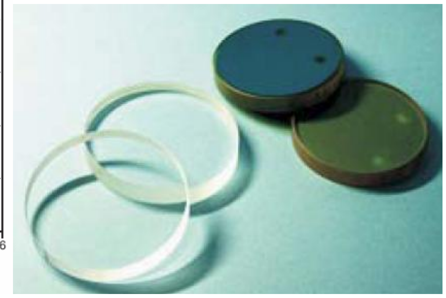
TruDefender

(right) Agilent Exoscan


D. **Beam Splitter** — Heart of FTIR — (typical: KBr/Ge for mid IR)







1. Modulation efficiency: varies as (2RT)I — max for R = 0.5 where (R+T) = 1

   ideal: $I(\delta) = 0.5\ I(\nu) \cos(2\pi\nu\delta)$

   -- typical mid IR uses KBr coated with Ge to partially reflect IR (> 1.8 μ)

   -- note: alternately B/S can be polarized reflection.

   Polarizing B/S — Martin Puplett -- $I_p(\delta) = 0.5\ (\nu)\ [1 + \cos 2\pi\nu\delta]$

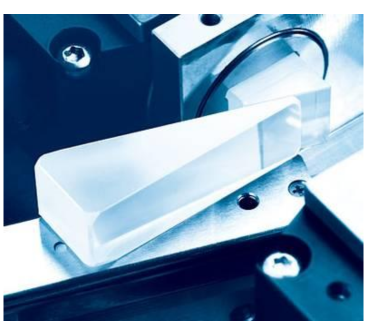
2. Other regions: coated quartz -- near IR -- change source

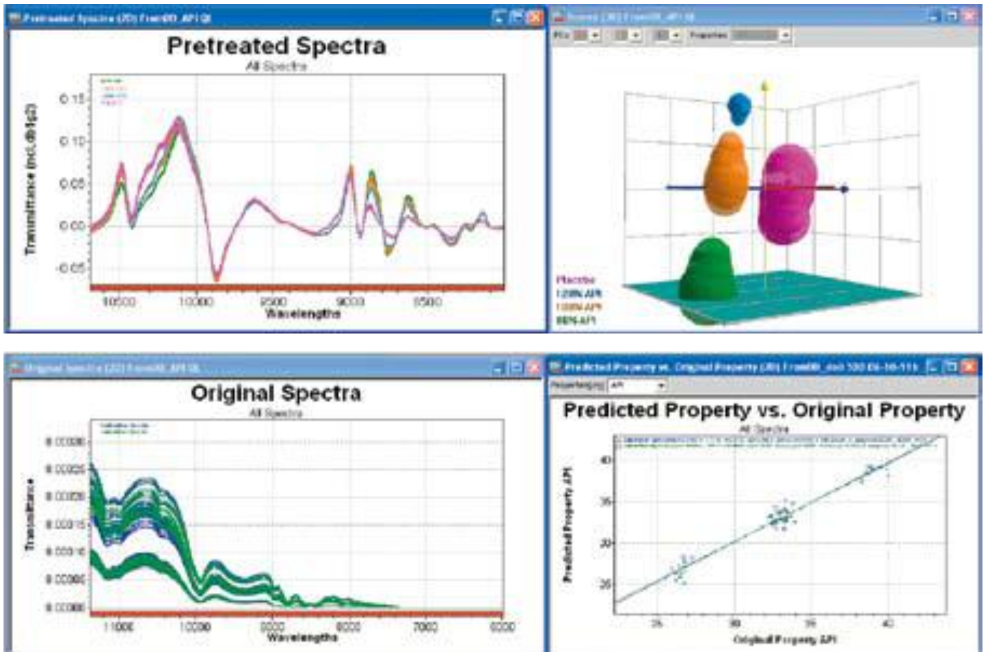
   mylar (must not accoustical couple to BS)-- far IR -- change detector

ASIDE:

*[*Near IR variations: Wiki: Near infrared spectroscopy is based on molecular overtone and combination vibrations. Such transitions are forbidden so the molar absorptivity in the near IR region is typically quite small. One advantage is that NIR can typically penetrate much farther into a sample than mid infrared radiation. Near infrared spectroscopy is therefore not a particularly sensitive technique, but it can be very useful in probing bulk material with little or no sample preparation. The molecular overtone and combination bands seen in the near IR are typically very broad, leading to complex spectra. Multivariate (multiple wavelength) calibration techniques (e.g., principal components analysis or partial least squares) are often employed to extract the desired chemical information. Calibration samples and application of multivariate calibration techniques is essential for near infrared.]

Buchi uses birefringent quartz wedges for interferometer, no beam splitter, polarizing the light in and out at 45^o makes the intensity modulate for each wavelength as wedge moves





Brimrose goes for portable design,
uses AOTF to create spectrum

Zeltex makes portables,
each targeted at an application

E. **Sampling** is big issue in IR -- solvent interference -- need for short path – [UK slides, link]

1. Gas -- [multipass cell] (better with tune laser)

Gas cell heated

demountable

demount liquid

refillable

vary path

ATR long crystal

Flow cells

minature

Cards salt substrates

PE substrate

ATR single bounce



KBr Pellet press   hydralic press split pea ATR   Harrick and   PIKE DRIFTS setup

2. Liquid — short path/salt — KBr/CaF_2/ZnSe … window & spacer

-- solvent must not dissolve cell / restrict region

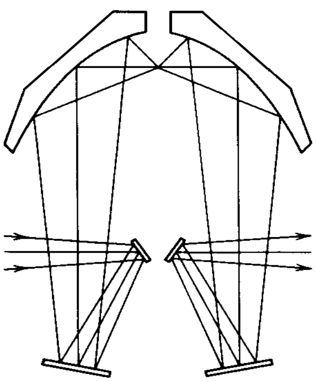
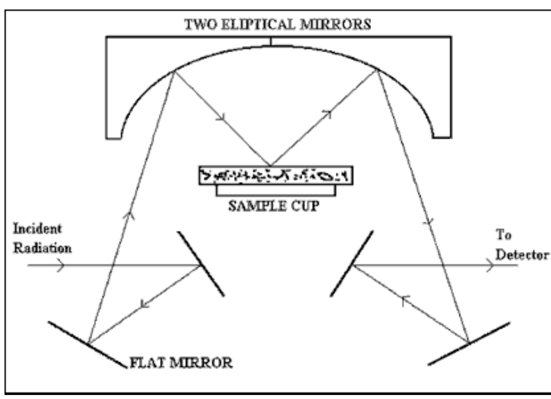
-- path from interference fringes $b = n/2(\Delta\nu)$ →(Fig 14-15)

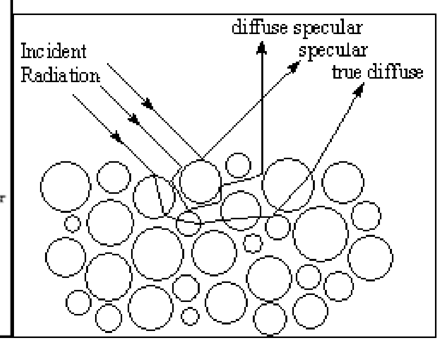
3. Small sample — beam condenser

-- microscope big appl now/autovials/bio

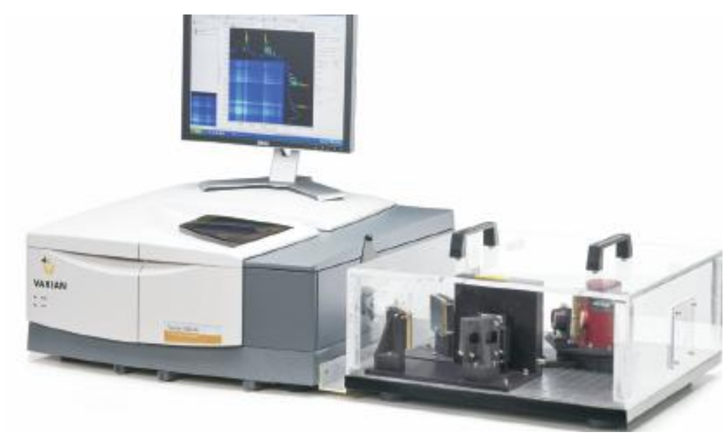
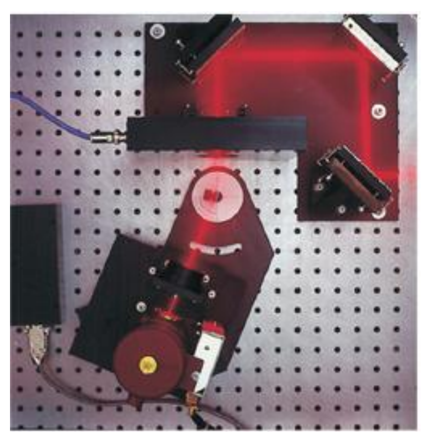
-- solids reflection — diffuse — powder — specular — IRAS surface and interface study

4. Can also be used with GC and HPLC as detector, not very sensitive, need long path or trick

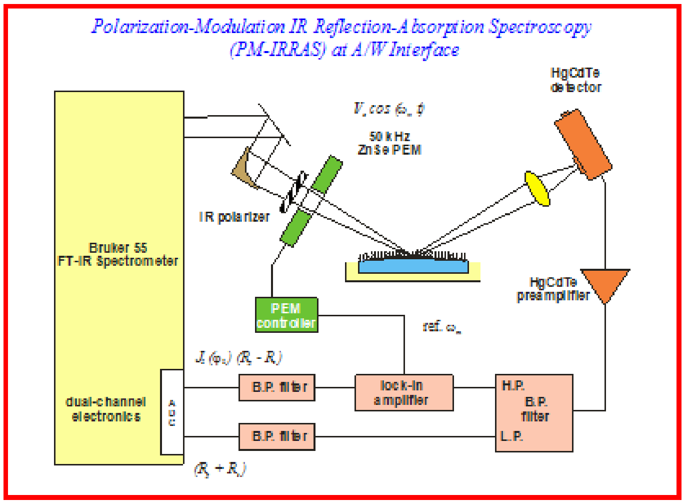



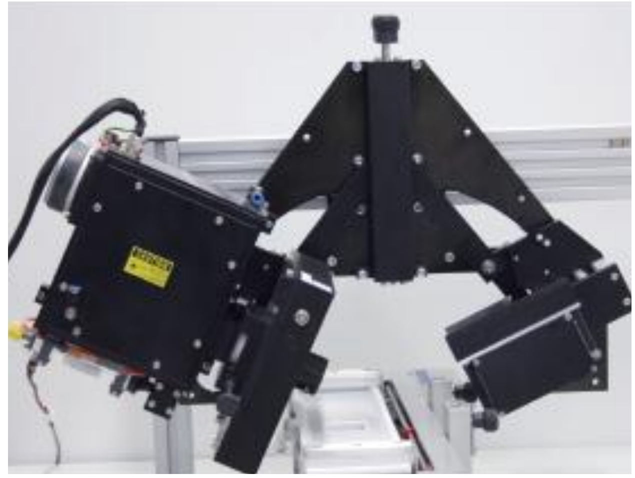


micro IR, shrink beam focus   DRIFTS (diffuse reflectance) idea, collect diffuse light, big mirror

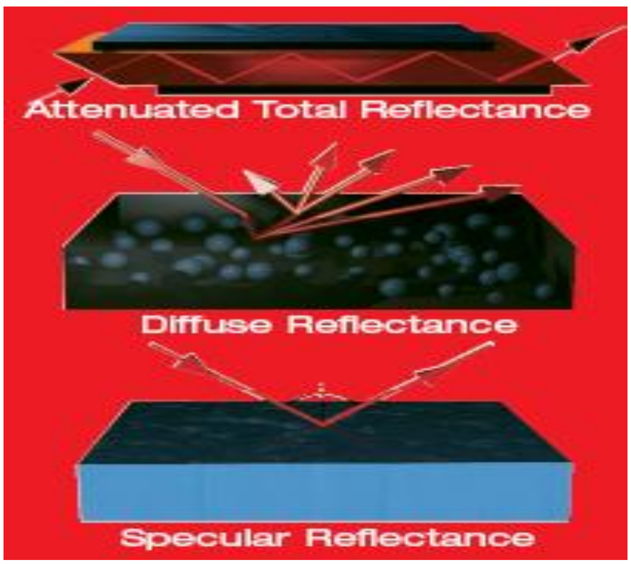



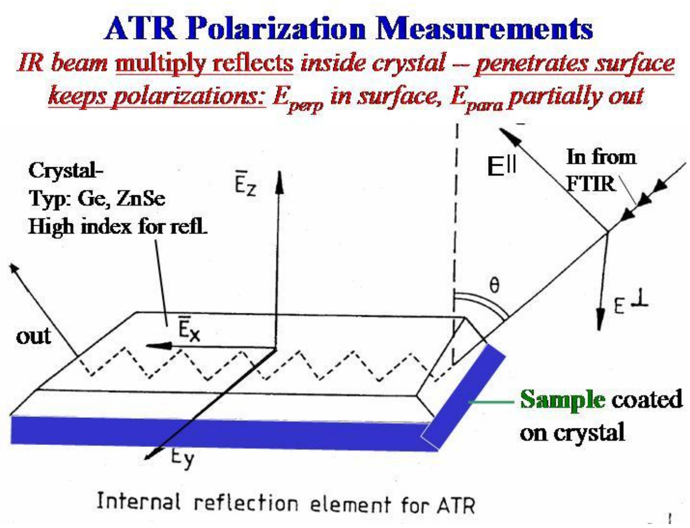
IRRAS setup often in separate compartment, control angle.   With metal substrate, grazing reflect best

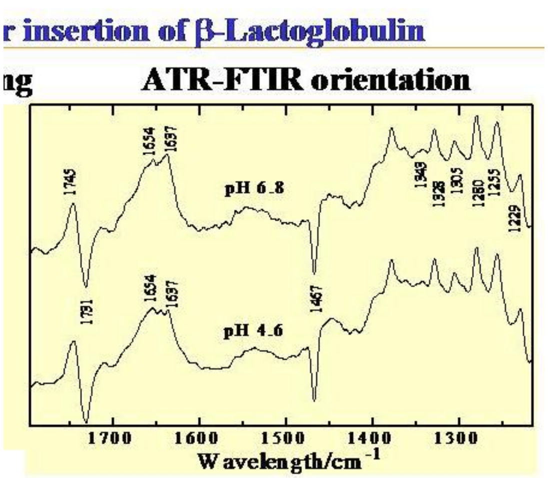




IRAS on an L-B water trough, can look at surface species, like proteins or lipids, separate form solvent





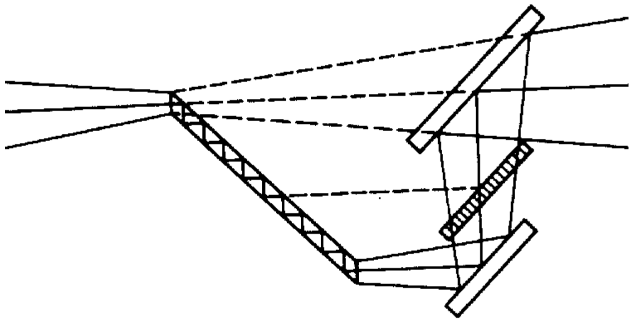


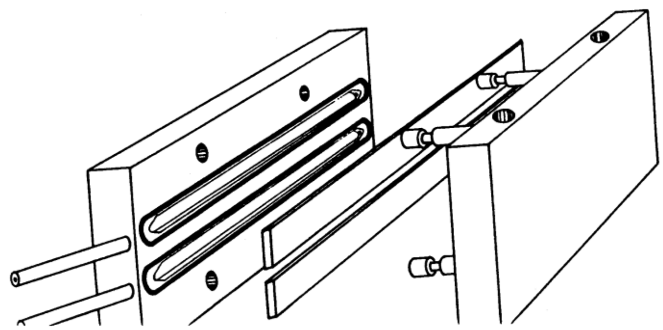
α-helix ⊥ Membrane surface

Zhang & Keiderling, Biochemistry 2006

Differential polarization measurement can yield orientation of an oscillator (dipole transition) and from that can derive orientation of molecule on a surface, using ATR, some specular reflection experiment, or oriented sample transmission, also can increase sensitivity → polarization modulation (Linear Dichroism)

Example, protein insert in lipid bilayer, determin helix orientation by comparison to lipid vibration polarization





ATR – couple light into crystal, in sample compartment   Flow ATR compare dynamics/equilibrium

5. Big use now days is microscopy, chemical and spatial identification

Microscopy/imaging

Single point data, aperture limit
Image is spot-to-spot sequential

Imaging system uses focal plane array detectors

Point is to chemically distinguish analyte with spatial resolution
Concept old, now wide spread. Problem - **resolution** limit, favor Raman
Array detectors permit very fast images with spatial rsolved spectra

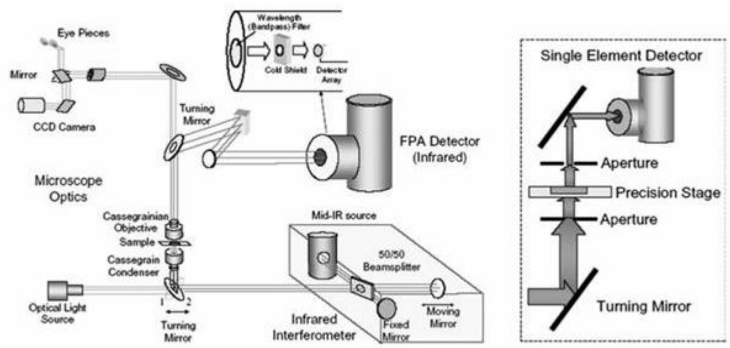
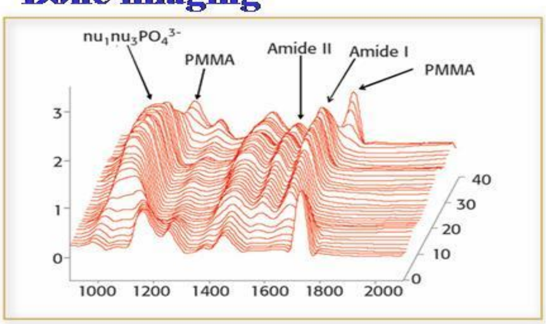


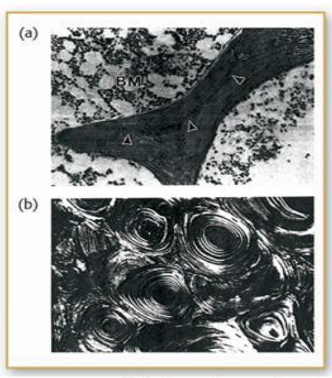
Figure 1 The configuration of a Fourier transform infrared (FTIR) spectroscopic imaging device consists of an interferometer coupled to a microscope and IR-sensitive focal plane array detector. When a conventional, single-element detector is employed (*right*), the microscope is necessarily equipped with apertures and a precision stage. For multichannel detection (*left*), no apertures are required.

FOURIER TRANSFORM INFRARED VIBRATIONAL SPECTROSCOPIC IMAGING: Integrating Microscopy and Molecular Recognition Ira W. Levin and Rohit Bhargava Annu. Rev. Phys. Chem. 2005. 56:429–74

Bone imaging



IR fingerprints change at each location in the tissue. Key: PMMA: polymethyl-methacrylate; amide I and amide II bands.



Images of (a) trabecular and (b) cortical bone.

Paschalis, . . . Mendelsohn, *J. Bone Mineral Res.* 19, 2000–(2004)
A. L. Boskey, . . . R. Mendelsohn, *Osteoporosis Int.* (in press).

PerkinElmer Spotlight (microscope

image by scanning a linear array of detectors – like raster scan)

F. **Applications**

1. Qualitative Analyses — major use

    -- group frequencies characterize band pattern
    -- library searches identify compounds

2. Quantitative — problem low ε, short path (due to solvent)

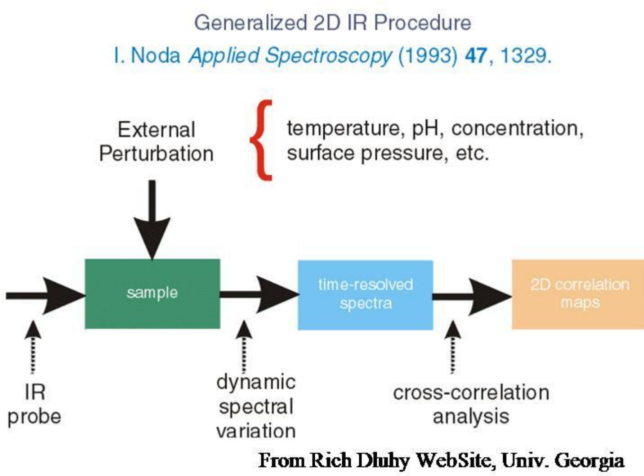
3. Noise limit — typically Johnson: $\sigma_A/A \sim \sigma_{0t}/E_r$ (-1/TlnT)

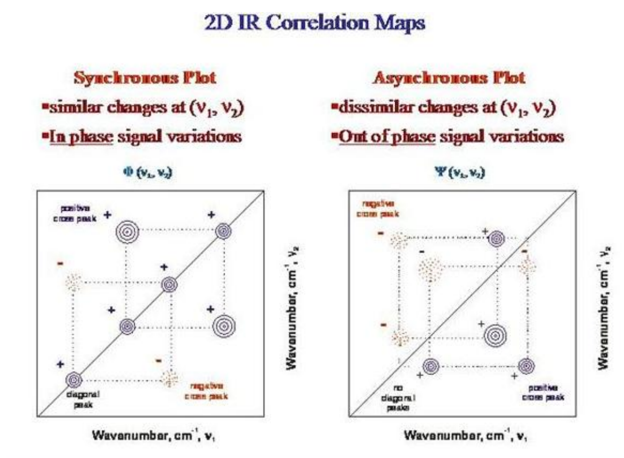
G. FTIR can get great S/N, $>10^3$ for $A > 0.1$

1. Baseline correction (single beam) precise subtraction (incl. H_2O, CO_2 vapor)

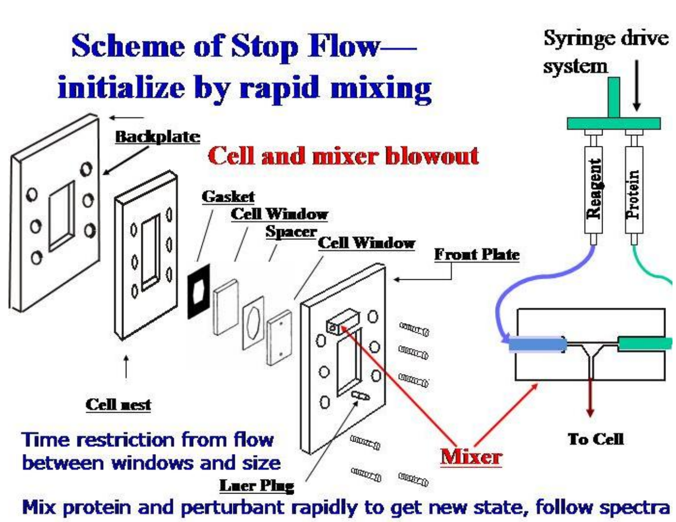
2. Resolution enhance — 2nd derivative

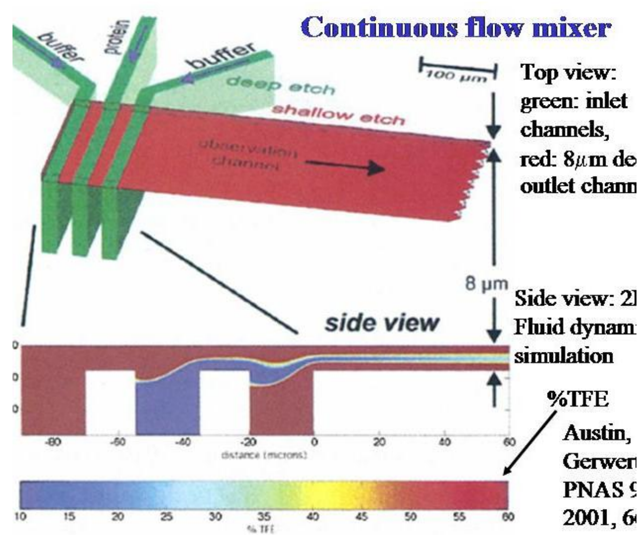
    -- Fourier self-deconvolution (emphasize high res part)
    -- Component fitting

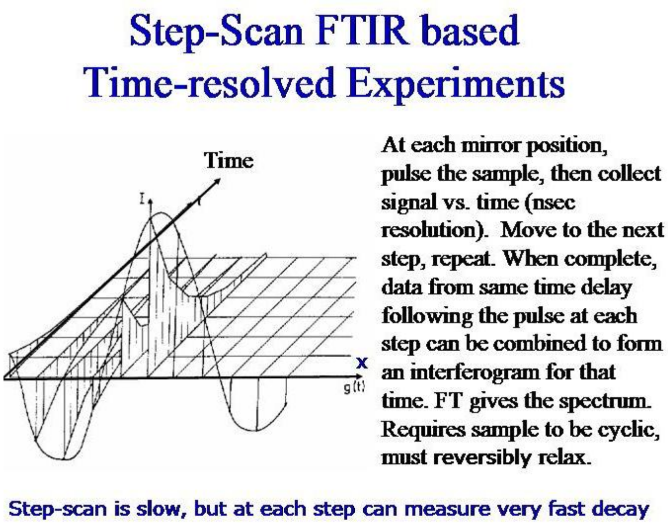


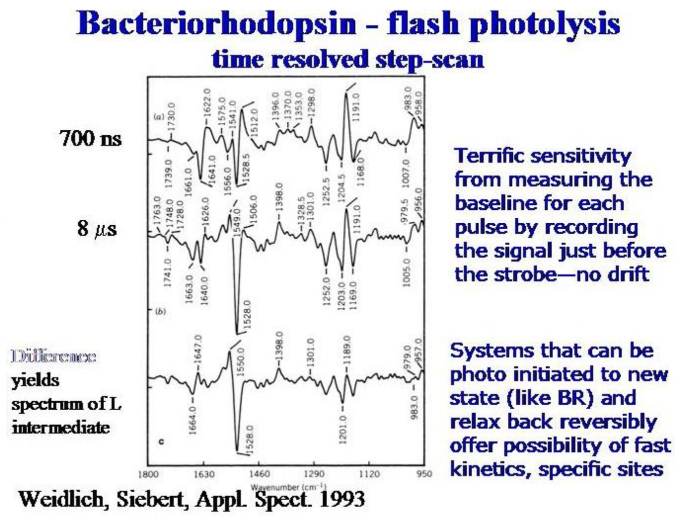


Kinetics









H. **Accessories**

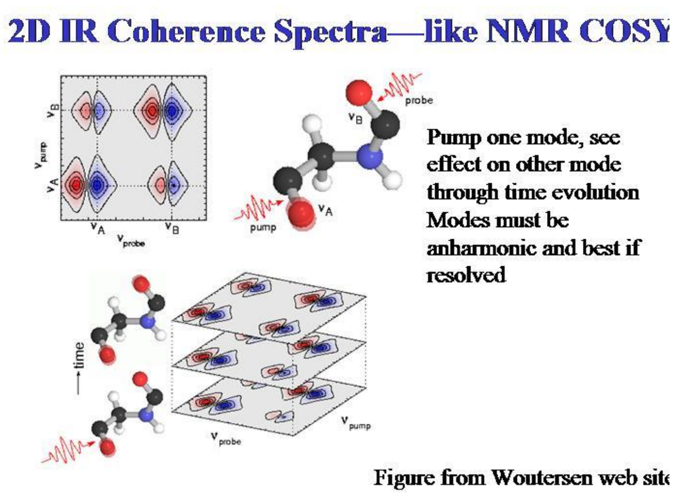
1. ATR — sample absorbance close to surface of all through reflectance/evanescent wave penetration, can study films, liquids (solutions) or flow

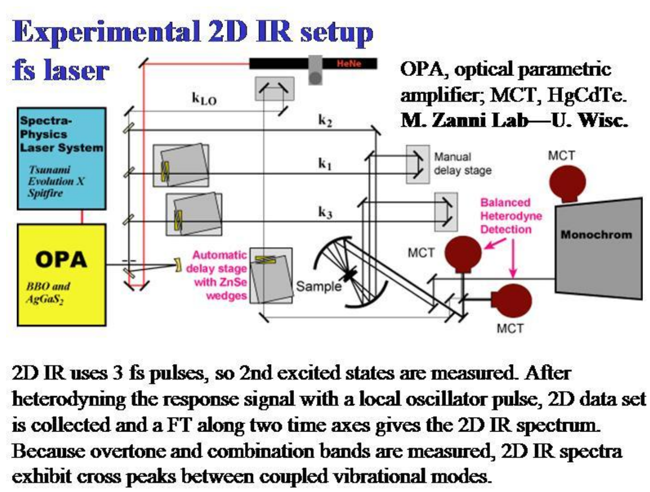
2. GC/LC detection — 2D idea -- spectrum for each chromatographic peak — qualitative analysis of components--identification

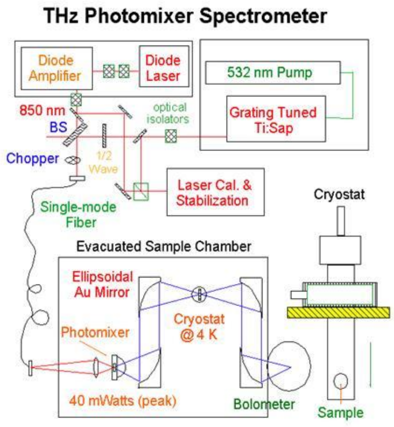
3. Microscope — multichannel detector (MCT array detector) -- 3D ideal spectrum for each image pixel -- qualitative analysis

4. 2-D correlation spectra — perturb sample observe changes in phase with perturbation

5. 2D-IR coherence spectra are more like COSY in NMR, register anharmonic coupling

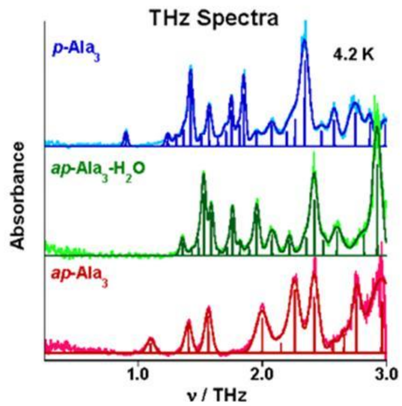




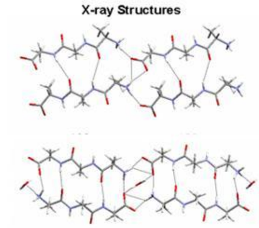


T.M. Korter and D.F. Plusquellic, Chem. Phy. Lett. 385 45-51 (2004

NIST cw THz spectrometer. The system consists of a low-temperature-grown GaAs photomixer driven at the difference frequency of two near-infrared lasers. The two lasers include a fixed frequency diode laser operating near 850 nm and ($\Delta\nu_{FWHM}$ ~ 0.0001 cm^{-1}) and a standing-wave Ti:Sapphire (Ti:Sapp) laser having a resolution of ($\Delta\nu_{FWHM}$ 0.04 cm^{-1}). The laser is seeded by feedback from an external grating-tuned cavity for absolute frequency stability.



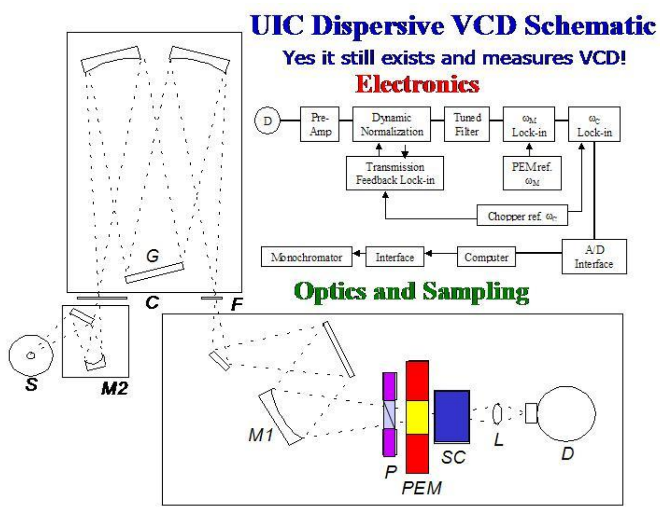
X-ray structures of the parallel (top) and anti-parallel (bottom) β-sheet forms of trialanine.

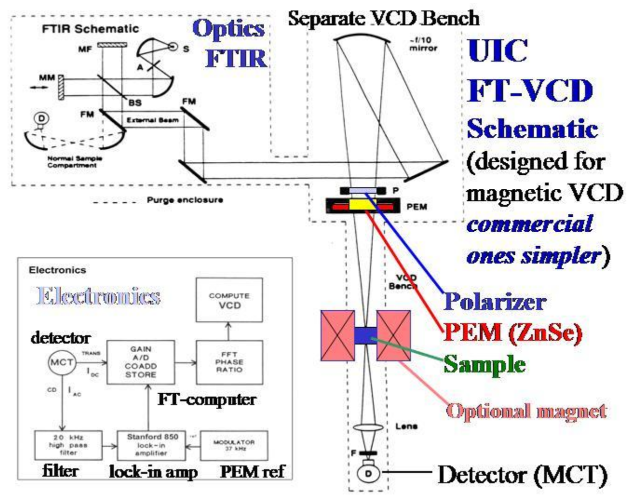


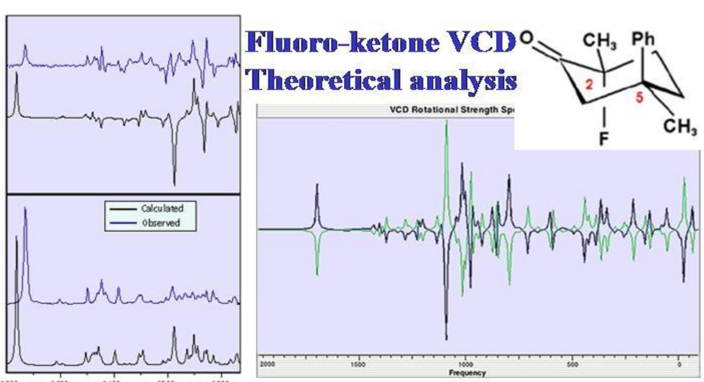
THz spectra of three crystalline forms of Ala3. All three are unique and illustrate the sensitivity in this region to changes in the β-sheet form and the co-crystallized water weakly bound in the lattice.

THz spectra in region below 100cm^{-1}, sense lattice fluctuations, large amplitude motions

Polarization modulation—get chirality/conformation with circular dichroism (VCD) (LD → orientation)



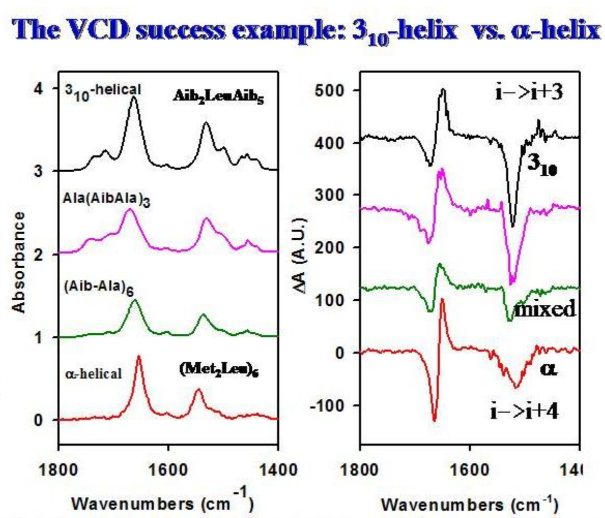




Comparison of the observed and calculated IR (bottom) and VCD (top) spectra for the (R,R) enantiomer.

Predicted VCD spectra for the (R,R) and (S,S) enantiomers (blue and green, respectively).

P. J. Stephens, Gaussian Web Site



Relative shapes of multiple bands distinguish these similar helices

Silva et al. Biopolyme

VCD introduces polarization modulation, senses chiral aspects of molecules, drug configuration analysis