XII. Infrared Spectroscopy — (Read Chap 14)

A. Regions: -- near IR (800-2500 nm — quartz optics/W-I lamp, diode detect)
   anharmonic vib, overtone and combination bands.
   -- mid IR (2500-20000 nm, 2.5-20μ, 400-500 cm$^{-1}$)
      (glowers, diode on TGS det, FTIR best, salt optics)
      fundamental vibrations, fingerprint pattern in vibrational modes.
   -- far IR (20μ -> , 400 cm$^{-1}$ -> )
      (difficult sources, detector, S/N) torsions, lattice vib, large amplitude mode

B. Dispersive IR (still find around, rarely made new)
   -- same principle as uv/vis double beam
   -- chop between ref and sample, meas. Difference
   -- multiple gratings/filters to cover range
      - scale sometimes change, near to mid-IR

   --same idea as diode array uv-vis spectrom.
   --detector 2-D can do ref and sample simult.
homemade for special purposes (TAK group) - modulation or kinetics measurement,

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

Experimental set-up of the T-Jump spectrometer at Frankfurt; CW infrared probe beam (red line); Pump beam (1909 nm, 10ns) to induce a T-Jump in the sample (7-10°C) (purple line); data acquisition by MCT detector and transient recorder (not shown)
C. Fourier Transform — (dominate all usage now and commercial market, single beam) - REVIEW

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

--(**old white light fiducial mark, current method count laser fringes**)
Research level FTIR instruments, all work very well:

Varian (Digilab) 660  Perkin-Elmer 400  Bruker Tensor,  Vertex  High Resolution

- unusual designs — swing, PE 1700 (pivot), Genzel, 1800 (double B/S), Bomem DA (vertical drop), Bomem Michelson (pivot), sliding wedge
RECALL: mini spectrometers now a big market issue:

Bruker Alpha, 30 x 22 cm  Thermo (Nicolet) S-10, variable sample chambers  JASCO similar
BOMEM bit bigger yet compact, see inside at:  http://www.mb3000ftir.com/html/quicktour.html

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

   --note: 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° 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 a big issue in IR -- solvent interference -- need for short path – [UK slides, link](#)

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

   ![Gas cell heated](image1) ![demountable](image2) ![liquid](image3) ![refillable](image4) ![vary path](image5) ![ATR long crystal](image6)

   ![Flow cells](image7) ![minature](image8) ![Cards salt substrates](image9) ![PE substrate](image10) ![ATR single bounce](image11)

   ![KBr Pellet press](image12) ![hydraulic press](image13) ![split pea ATR](image14) ![Harrick](image15) ![PIKE DRIFTS setup](image16)

2. Liquid — short path/salt — KBr/CaF$_2$/ZuSe … [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

5. Big use now days is **microscopy**, chemical and spatial identification
Diffuse reflectance setup, eliminate specular, older

DRIFTS idea, collect diffuse light, big mirror

IRRAS setup often in separate compartment, control angle. With metal substrate, grazing is best
IRAS on an L-B water trough, can look at surface species, like proteins or lipids

**Lipid bilayer insertion of β-Lactoglobulin**

**Fluorescence quenching**

\[
\frac{I_0}{I} = 1.0 + k \cdot [Q]
\]

At pH 6.8 & 4.6, 4 & 6 nm blue shift in \( \lambda_{\text{max}} \)

**ATR-FTIR orientation**

Zhang & Keiderling, Biochemistry 2006
ATR – couple light into crystal, in sample compartment

Flow ATR compare dynamics/equilibrium

**Microscopy/imaging**

- Single point data, aperture limit
- Imaging system uses focal plane array detectors
- Image is spot-to-spot sequential
- Point is to chemically distinguish analyte with spatial resolution
- Problem – resolution limit, favor Raman
- Array detectors permit very fast images with spatial resolved spectra

**Bone imaging**

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

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

F. Applications

1. Qualitative Analyses — major use
   -- group frequencies characterize band pattern
   -- library searches identify compounds

2. Quantitative — problem low $\varepsilon$, short path (due to solvent)

3. Noise limit — typically Johnson: $\sigma_A/A \sim \sigma_0/E_r (-1/T\ln T)$

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

1. Baseline correction (single beam) precise subtraction (incl. H$_2$O, CO$_2$ vapor)

2. Resolution enhance — 2nd derivative
   -- Fourier self-deconvolution (emphasize high res part)
   -- Component fitting

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Kinetics

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**Scheme of Stop Flow** — initialize by rapid mixing

**Continuous flow mixer**

Top view: green: inlet channels, red: 8$\mu$m de outlet channel

Side view: 2 Fluid dynam simulation

Austin, Gerwer
PNAS 2001, 6
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

**2D IR Coherence Spectra**—like NMR COSY

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**Step-Scan FTIR based Time-resolved Experiments**

At each mirror position, pulse the sample, then collect signal vs. time (ns to ms resolution). Move to the next step, repeat. When complete, data from same time delay following the pulse at each step can be combined to form an interferogram for that time. FT gives the spectrum. Requires sample to be cyclic, must reversibly relax.

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**Bacteriorhodopsin - flash photolysis**

**time resolved step-scan**

Terrific sensitivity from measuring the baseline for each pulse by recording the signal just before the strobe—no drift

Systems that can be photo initiated to new state (like BR) and relax back reversibly offer possibility of fast kinetics, specific sites

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**Weidlich, Siebert, Appl. Spect. 1993**

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**Figure from Woutersen web site**

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**Experimental 2D IR setup**

OPA, optical parametric amplifier, MCT, HgCdTe. M. Zanni Lab—U. Wisc.

2D IR uses 3 fs pulses, so 2nd excited states are measured. After heterodyning the response signal with a local oscillator pulse, 2D data set is collected and a FT along two time axes gives the 2D IR spectrum. Because overtone and combination bands are measured, 2D IR spectra exhibit cross peaks between coupled vibrational modes.
THz spectra in region below 100 cm\(^{-1}\), sense lattice fluctuations, large amplitude motions.

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