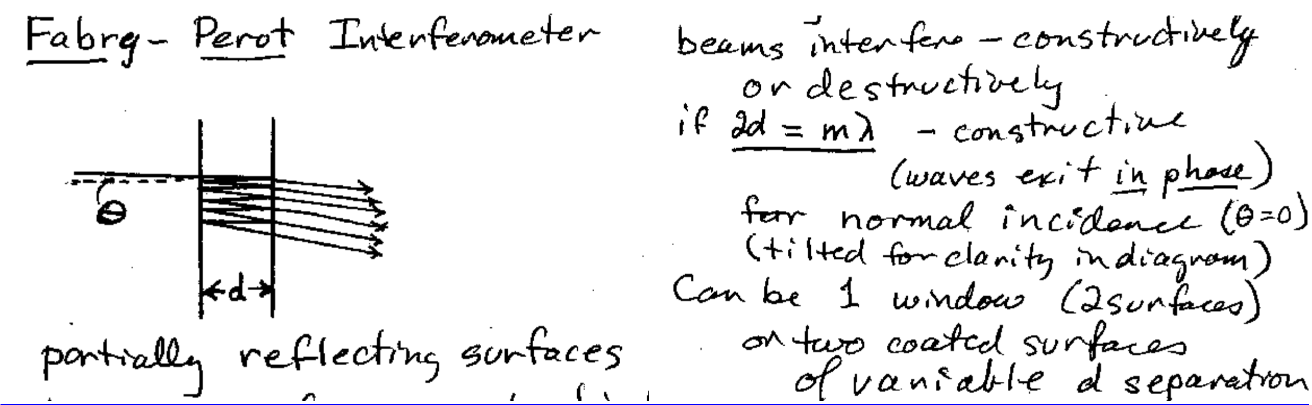
Chem 524 Lecture notes (Sect. 7)—update 2013

IV. Wavelength Discriminators (continued)

B. Interferometers (A selection of old notes/handouts can be linked here)

1. Fabry-Perot (text: Sect. 3-7, Figure 3-56)



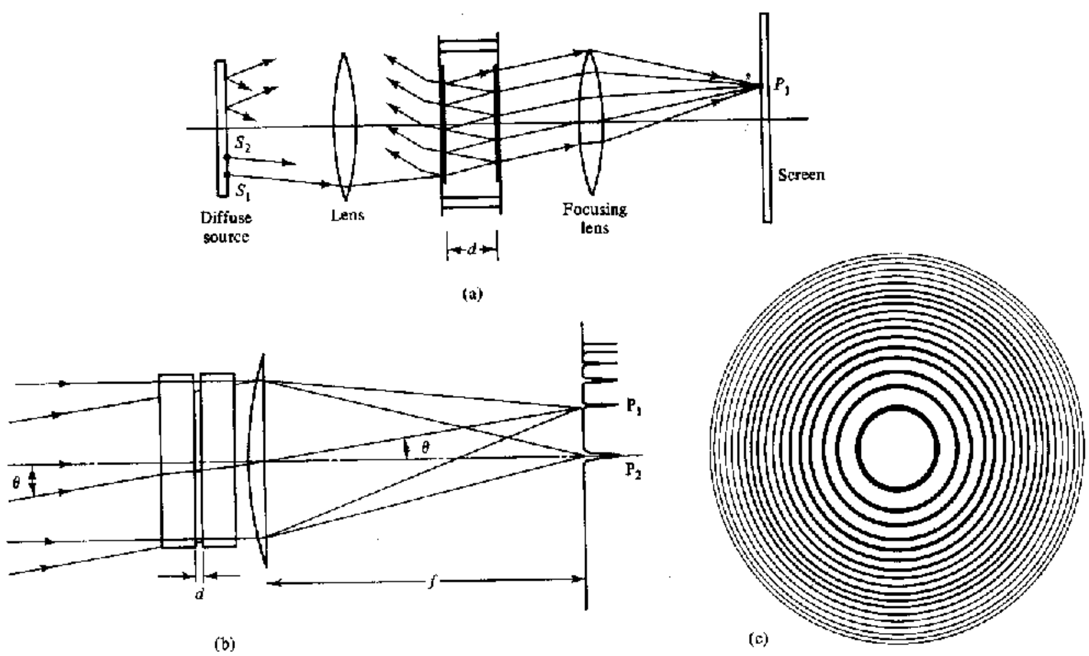
— multiple passes between partially reflecting surfaces, *m large #,* fit real device

— parallel, perpendicular ray - if path (gap) d equals m(λ/2) — constructive interference

-– free spectral range: **$\Delta\lambda = \lambda/(m+1) \sim \lambda/m = 2d/m^2 = \lambda^2/2d$** — normal incidence

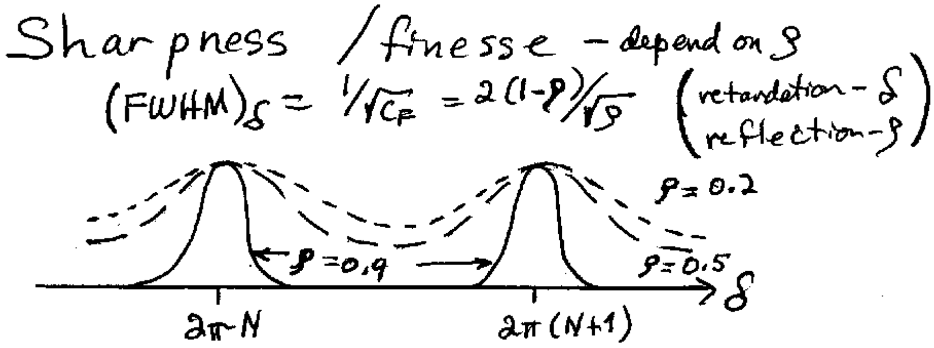
— if *beam enters at angle* lead to "fringes" , because spacing changes: **$m\lambda = 2d \cos\theta$**

Work Out geometry -when reflected beam differs from straight through path by nλ/2 get minimum (destructive) or by nλ (get maximum - constructive), *positions of fringes vary as spacing or λ changes,* this will vary with angles so for *single λ fringes go out like rings at θ*



sharpness of interference depends on reflectivity (coefficient of finesse): $C_F = \rho/4(1-\rho)^2$

see C_F increase as ρ increases, FWHH ~ $(C_F)^{-1/2}$ – but costs transmission



Resolution very high, C_F, but *must add element to eliminate m+1 and m-1* waves, etc., $\Delta\lambda$ on d

e.g. at λ = 400 nm and d = 1 mm, m~5000, so m+1 would separate by $\Delta\lambda$ ~ 0.08 nm

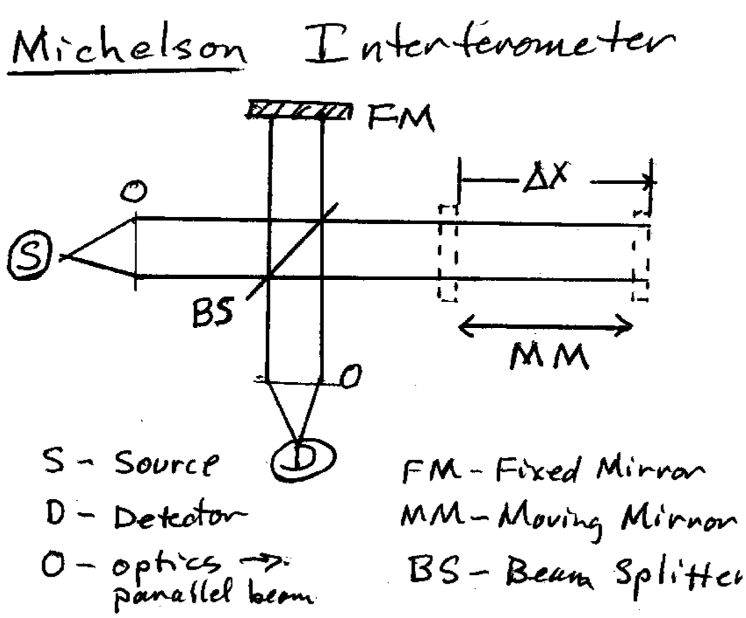
use: — couple to monochromator, which can sort the m's→ enhance resolution to $\Delta\lambda_i$

— etalon in laser cavity can select mode — narrow output line, multiple ones select

2. Michaelson Interferometer (ref: see Griffiths & DeHaseth Chap 1, and/or Marshall & Verdun)

–note our Textbook is a little different, tied to frequency, which is not the issue--emphasize)

You will need to go beyond the text for this section – often on cumes!!



encode frequency ($\tilde{\nu}$, ***wave number***) by ***position (Δx)*** of moving mirror, interference at beam splitter after recombining beams reflected from moving and fixed mirrors creates (interferogram) *signal, S(x)*

Δx created by *motion of mirrors*

if move at constant speed, encode by modulation frequency, $f = \mathbf{2}\upsilon\tilde{\nu}$

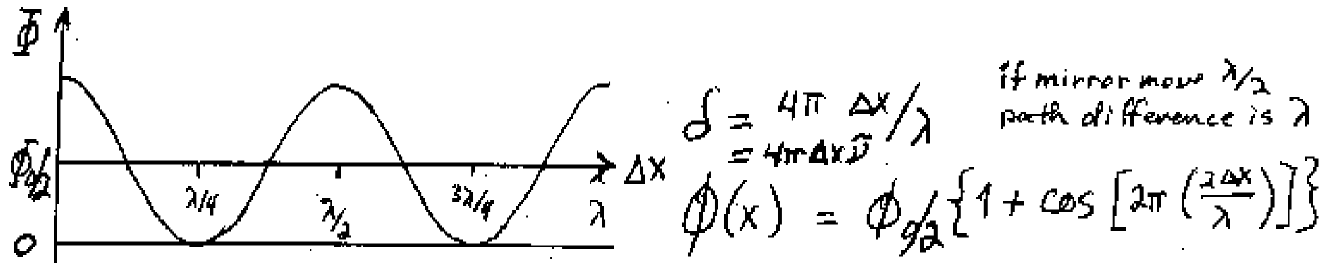
interpret: obtain *spectrum, $B(\tilde{\nu})$,* by *Fourier transform of intensity*, S(x) (response) vs. Δx

$$\mathbf{B(\nu) = \int S(x) \cos[4\pi\nu\Delta x]\, dx}$$

a. Monochromatic light — interferogram is sine wave - $\Delta x = 0$, S(x) maximum, both arms same length, in phase, $\Delta x = \lambda/2$ again in phase (recall path increase by $2\Delta x$)

$$\phi(x) = (\phi_0/2)\{1+\cos[2\pi(2\Delta x/\lambda)]\} \rightarrow S(x) = (\phi_0/2)\cos\delta \quad \delta = 2\pi(2\Delta x/\lambda) - \textit{retardation}$$

note: *S(x) only keeps track of modulated part*, there is DC offset of $\phi_0/2$ (seem wasted?) factor of 2 - *half the light is returned to source*, not lost, 180^o out of phase, *~(1 - cos δ)*



retardation — measure path difference waves: $\delta = 2\pi(2\Delta x/\lambda) = 4\pi\tilde{\nu}\,\Delta x$ *(units—radians)*

if move mirror at *constant rate*: **$\upsilon = dx/dt$** then interference

modulation frequency will be **$f = 2\upsilon/\lambda = 2\upsilon\nu/c = 2\upsilon\tilde{\nu}$**

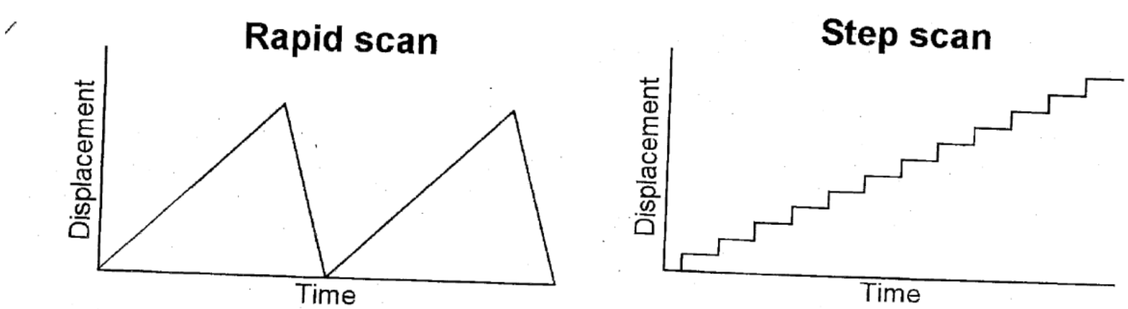
modulates signal: e.g. at $\upsilon = 0.6$ cm/sec for $\tilde{\nu} = 1600\ cm^{-1}$ → f = 1920 Hz

but see *lower wavenumber → lower mod frequency*, encode spectrum by $\tilde{\nu} \sim \Delta x$

Lab instruments are built to *sense the mirror position* (Δx) while moving *const. υ* but the modulation, f, provides *detection efficiency* (*AC detection*, see later section).

Spectra can also be collected by *stepping the mirror*: $x_0 \rightarrow x_0+\Delta x \rightarrow x_0+2\Delta x \rightarrow$ etc.

then the detection is "DC", works well for fast time-dependent processes



spectral response (F.T.): $B(\nu) = \int S(x)\cos[4\pi\tilde{\nu}\Delta x]\,dx = \int\{(\phi_0/2)\cos\delta\}\cos[4\pi\tilde{\nu}\Delta x]\,dx$

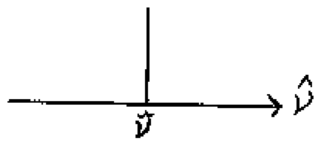
Note: this is *real transform*, more general *complex:* $B(\tilde{\nu}) = \int S(x)\exp[(4\pi i)\tilde{\nu}\Delta x]\,dx$

if x went to ∞ then $B(\tilde{\nu})$ would be a delta function at $\tilde{\nu}_0$, the laser wavelength: $\delta(\tilde{\nu}-\tilde{\nu}_0)$

but in a *real system* the mirror must stop, *Δx is finite* and if truncate scan at Δx_{max} this leads to a band/line shape for the spectrum : $G(\tilde{\nu}) = 4x_m\,\mathrm{sinc}(4\pi\tilde{\nu}x_m)$

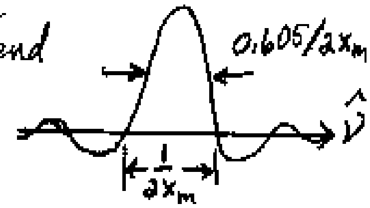
Note – many FTIR use HeNe to create this sine wave as a "ruler" to determine Δx during motion of mirror – $\Phi_0/2$ because half light back to source

If $\Delta x \rightarrow \infty$ then spectrum:



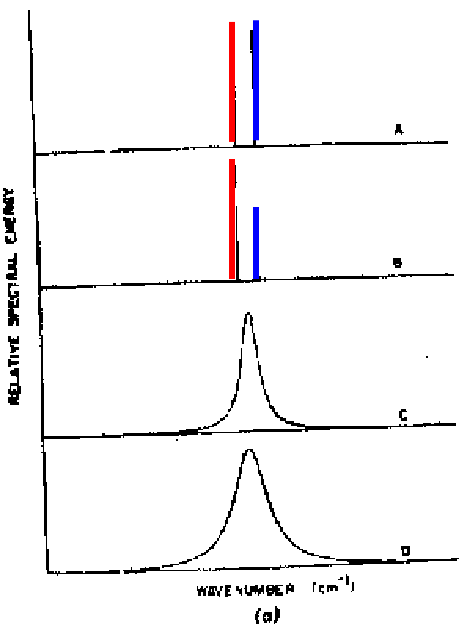
If $\Delta x \rightarrow x_{max}$

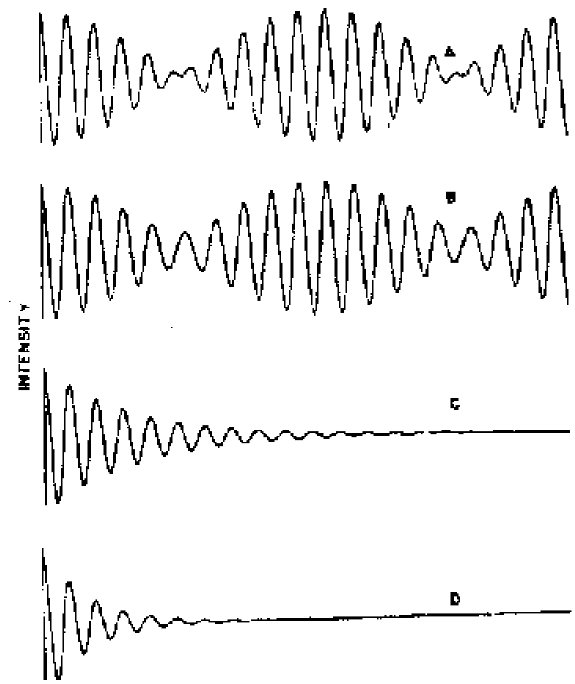
shape broaden
resolution depend on x_m



b. Polychromatic light: interference between different wavenumbers leads to envelope whose amplitude decays over interferogram oscillation with increase in Δx — reflect spectrum

Two frequencies–get *beat pattern* – amplitude decrease then increase again (like echo)

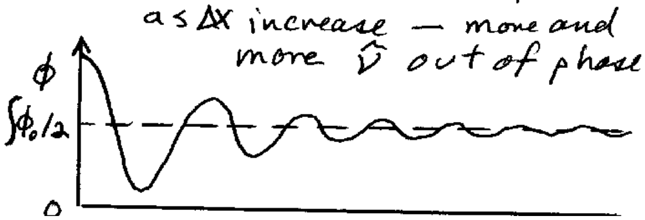




Broader spectrum, must integrate over all contributions, envelop decays:

$$S(x) = \int G(\tilde{\nu}) \cos(4\pi\tilde{\nu}\Delta x)\, d\nu$$

Many interferences — at $\Delta x = 0$ all in phase
as Δx increase — more and more $\hat{\nu}$ out of phase



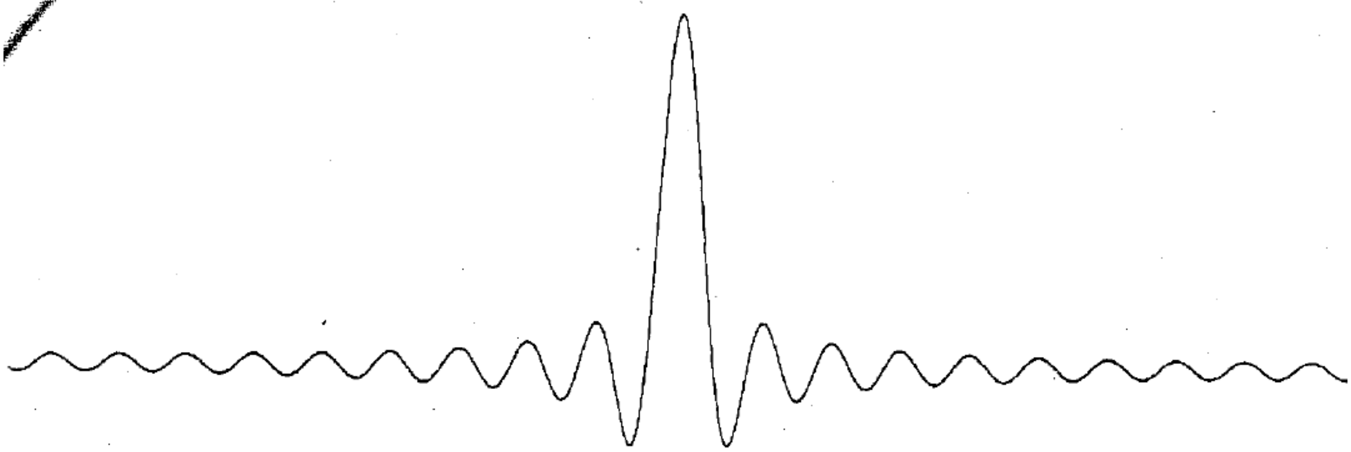
envelope of interferogram decays – note lots of light but not modulated — DC component carries no spectral information

Result: low Δx ~ rep. broad base line, high Δx ~ rep. interference of close frequencies

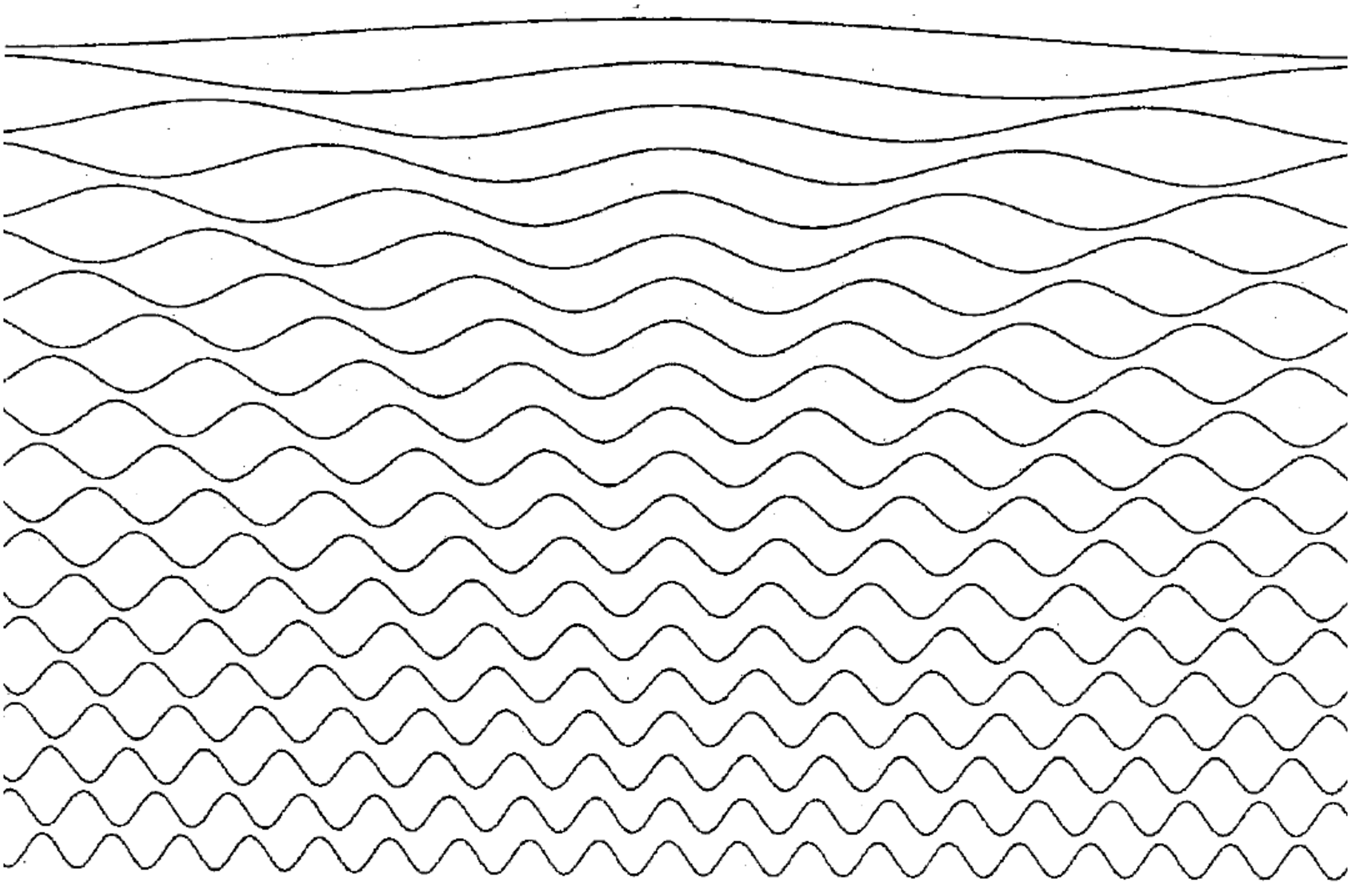
Broader spectra, B(ν), band decay faster (more peaked/defined "center-burst")

Few sharp bands create interferences that yield oscillations in envelop

Building an interferogram from component sinusoidal variations for individual wavenumbers These vary over a wide frequency range, the bottom one has 20 periods, and the top has 1 period in the range. This is like a spectrum form 4000 to 200 cm^{-1} → result is sharply peaked



Composite Signal

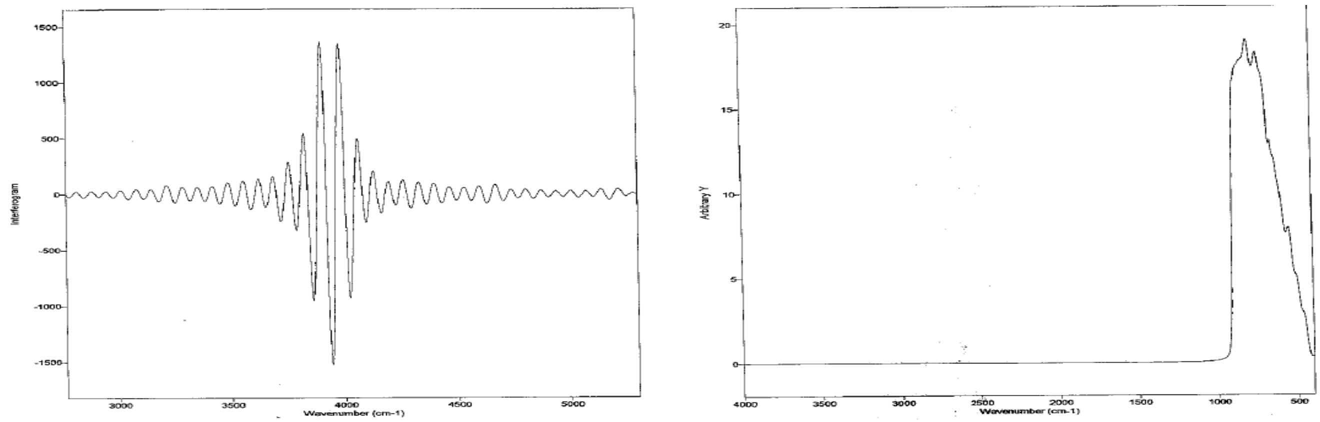


Component Sinusoids

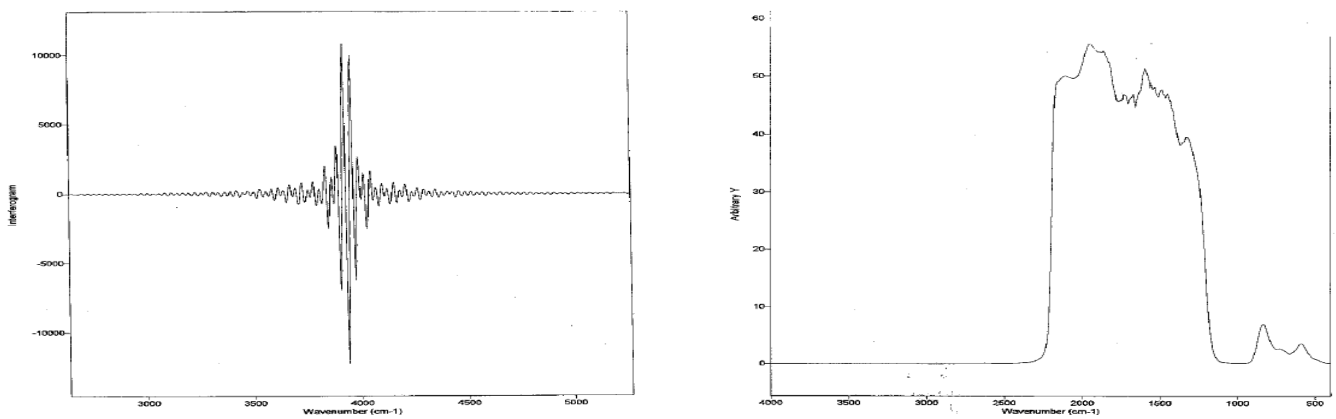
Interferogram shape: Broader band, faster decay, narrower slower (see more large amplitude)

frequency of oscillation due to the spectral range,

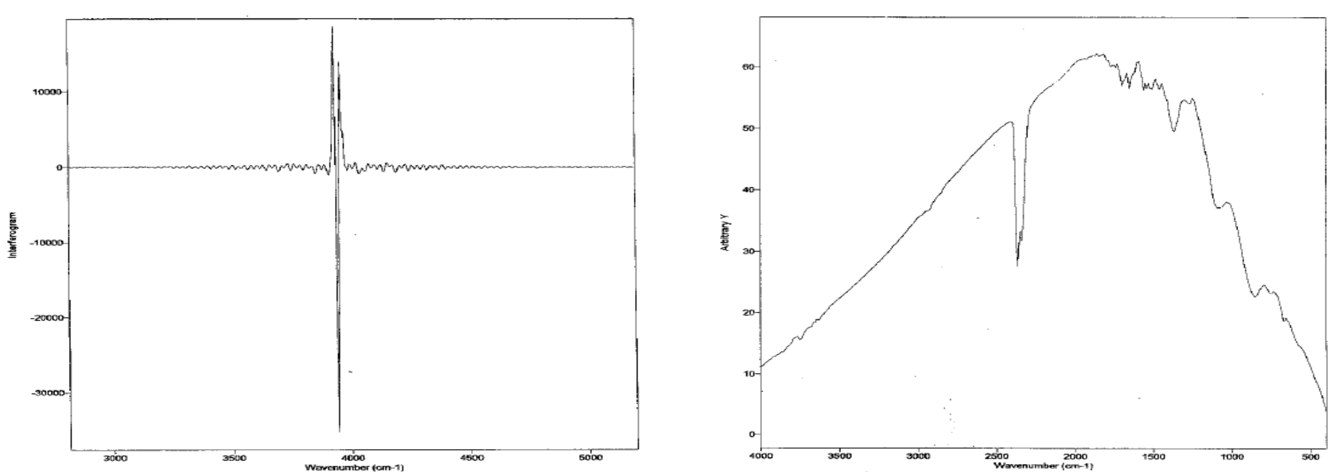
high wavenumber, near IR, faster changes in Δx, far-IR slower variation



(900-500 cm^{-1}) - Several big oscillation near centerburst then spread, slow decay with inc. Δx



(2200-1200 cm^{-1}) - Faster oscillation and decay, less intensity at higher Δx values, beat pattern develop – characteristic of structured spectrum – *symmetry less, phase cor. freq. depend-chirp*



(400-4400 cm^{-1}) - Broad band results in interferogram peaked at just one point, center burst spectral information actually in the variations of very weak parts to either side of centerburst requires high precision of digitization to get both parts of interferogram – *reduced symmetry*

resolution of components controlled by extent of mirror *displacement*

Finite motion of mirror — *limit resolution*, gives line after FT a bandshape (see above)

resolution — *ideal:* $\Delta\tilde{\nu} = (2x_m)^{-1}$ -- if Δx too small, then interference between close lying $\tilde{\nu}$ values does not modulate the interferogram intensity

(back 2 pages: *two sharp line* example – move $\Delta x \sim (\nu_1-\nu_2)^{-1}/2$ to get minimum)

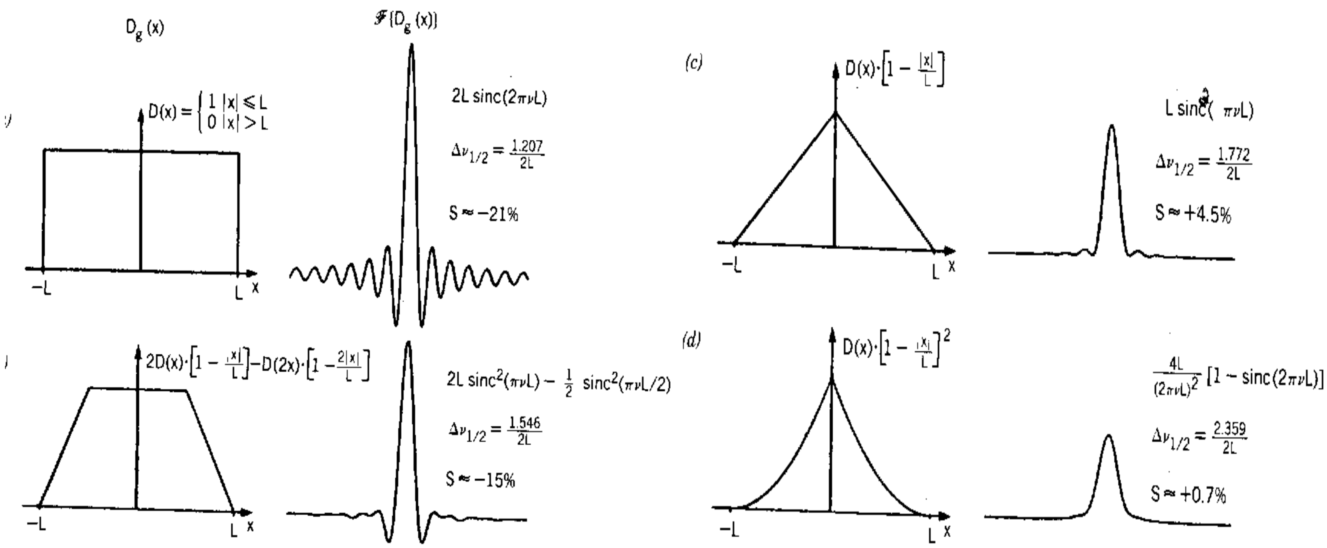
apodization – D(x) — modify bandshape by convolving D(x) with S(x), also lowers resolution

boxcar (no alteration, just truncation), triangular (linear ramp from $\Delta x = x_m \rightarrow 0$),

others (more continuous functions, i.e. *basic idea* is: $D(x) \rightarrow 0$ as $\Delta x \rightarrow x_m$)

--result is *boxcar* shape has sidebands (±), *triangular* makes them positive, but broaden FWHM, other functions similar, see example below

--idea is to minimize contribution at x_m, since that will be singularity (discontinuity)



Note: in these figs, L is $2\Delta x_m$ in above equations, boxcar and triangle, 0.6 and 0.88 Δx_m

c. FT Advantages – *need to know*

Jacquinot — no slit — throughput enhanced, but need small aperture high resolution

Fellgett — multiplex — all frequencies simultaneously detected

Connes — frequency accuracy (compare/correct spectra) – reference to laser line

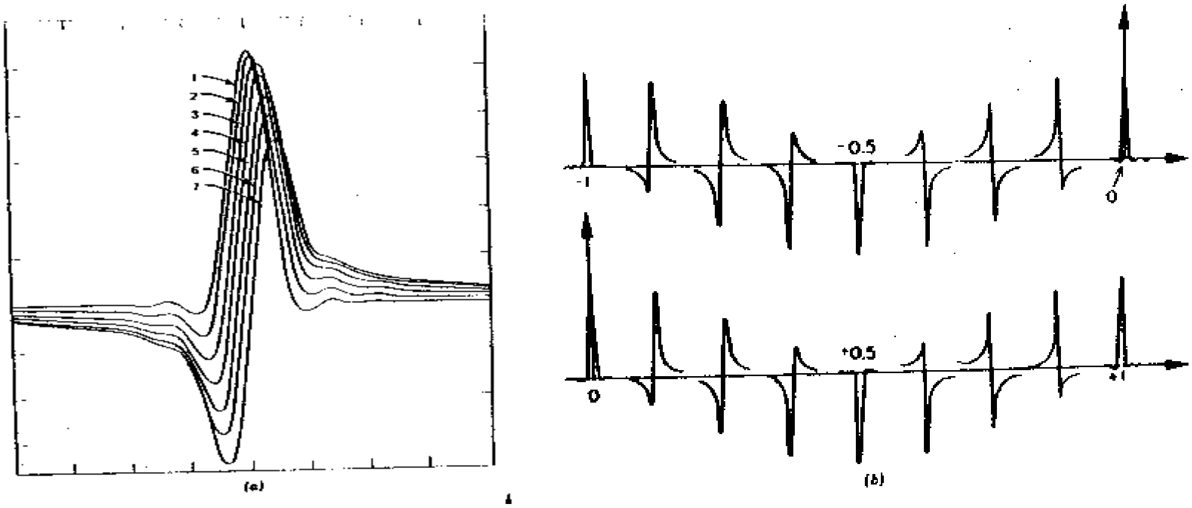
Costs: lose 1/2 light which returns back to source (out of phase) at Beam splitter

lack modulation depth (at large Δx values)– *only can transform modulation* –

implies → scanning mirror further has vanishingly small return after some point

noise normally constant in detector, but signal only S(x) or modulated part of $\phi(x)$

useful signal at high Δx (high res part) is relatively small compared to noise phase errors need correction/distort bandshape (here complex FT is important)



d. Phase correction

Digital signal meas. scan — can miss $\Delta x = 0$: $S(x) = \int B(\tilde{\nu}) \cos[4\pi\tilde{\nu}(\Delta x - \varepsilon/2)]\, d\tilde{\nu}$

Spectrum acts like had *constant phase shift* by $\varepsilon/2$ or S(x) *origin change* : $\Delta x - \varepsilon/2$
Thus appearance is same, just shifted along Δx axis

Electronic frequency response — $\varepsilon \sim \varepsilon(\tilde{\nu})$ — "chirp"--*lose symmetry at x=0*
Phase shift, $\varepsilon(\tilde{\nu})$, can depend on wavenumber, for *rapid scan* experiment
wavenumbers have $f = 2\upsilon\tilde{\nu}$, modulation frequency, detector, filters affect phase
See lobes before and after centerburst not same size, eventually flip signs

Result — S(x) has sine components — (or if conventionally computed, apparent $B(\nu)$ has distortion, not real spectrum) - evidenced (see above) by *derivative shapes*
Best separated by using *complex FT:* $\mathbf{B(\tilde{\nu}) = \int S(x) \exp[(4\pi i)\tilde{\nu}\Delta x]\, dx}$
Note S(x) contains the phase error, *measurement problem not spectrum*, $B(\nu)$.

Correct for phase — from complex FT derive: *Re ~cos(ε) and Im ~sin(ε)* components

If just digitization, could shift origin until the spectrum was all positive (NMR method)

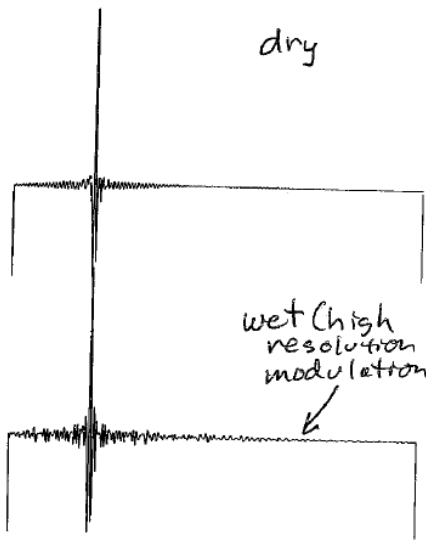
Mertz algorithm, get freq. depend. phase correction: $\varepsilon(\tilde{\nu}) = \tan^{-1}[\mathrm{Im}\, B(\tilde{\nu})/\mathrm{Re}\, B(\tilde{\nu})]$

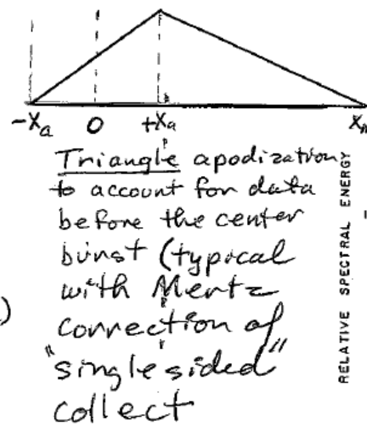
So need FT to correct FT! Solution: Measure sym. interferogram over small Δx range (assume $\varepsilon(\tilde{\nu})$ varies slowly with $\tilde{\nu}$), solve for $\varepsilon(\tilde{\nu})$ and use those values to correct phase

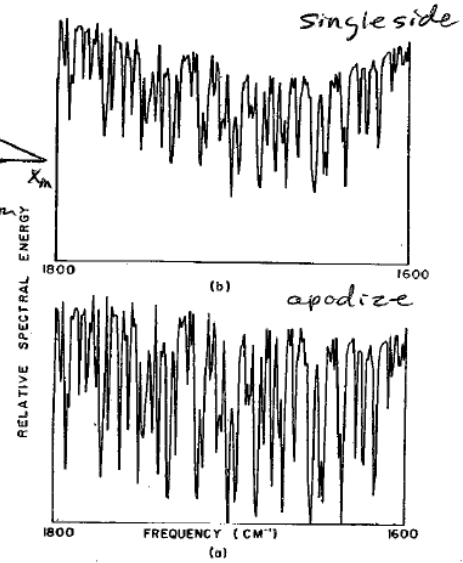
To carry out the complex FT, measure *both sides of centerburst* for a short region only (note impossible in FT NMR). Get correction and than can do asymmetric IF for high res.

If want to use all this data for final spectral calculation, Results would over sample centerburst, so use ramp function to correct apodization

Doing properly give better measure of baseline, i.e. broad band parts of spectrum







ig. 1.17. (*Above*) Interferogram measured from a fairly well purged instrument. If an ppreciable amount of water vapor had been present in the beam, modulations would be bservable in the interferogram at much higher retardation. (*Below*) Interferogram measured rom the same instrument with a sheet of 50-μm-thick polystyrene inserted in the beam. Note that the modulations die out at fairly low retardation because the bands of polystyrene re quite wide and do not require a large retardation to effect their resolution.

Fig. 1.18. (*Above*) Spectrum of water vapor computed from a single-sided interferogram that had not been weighted in the fashion shown in Fig. 1.16; note that none of the lines has a transmittance much less than 50% even though there is a large amount of water vapor in the beam. (*Below*) Spectrum computed from the same interferogram used for the spectrum above, but weighted with the correct apodization function.

e. Alignment error and Aperture — lower resolution

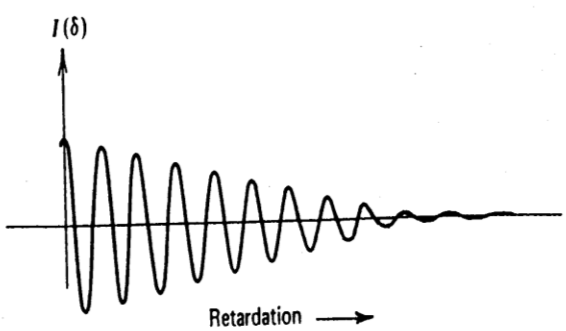
solid angle accepted: $\Omega = 2\pi\alpha^2 = 2\pi(\Delta\tilde{\nu})/\tilde{\nu}$ -- *resolution limited by parallelism*,

higher resolution, $(\Delta\tilde{\nu})/\tilde{\nu}$, need smaller Ω which requires smaller aperture

causes — lose modulation depth at large Δx (result lost resolution — like apodization)

concept → short wavelengths become more out phase as move mirror due to path differences in wider aperture/angles

also→ loss of frequency accuracy (*wavenumber shift*): $\tilde{\nu}' = \tilde{\nu}\,[1-\Delta\tilde{\nu}/4\tilde{\nu}]$



1. Appearance of the interferogram of a beam of monochromatic radiation diverging as it passes through the interferometer.

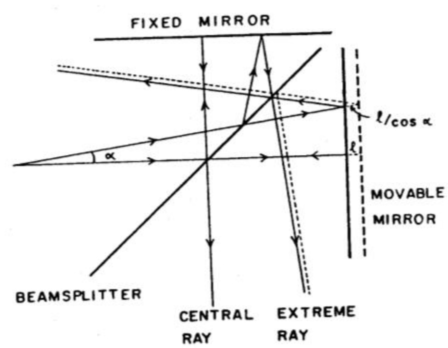
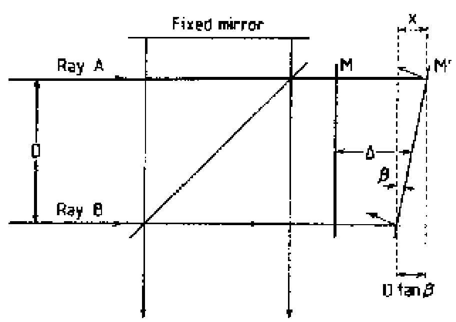


Fig. 1.20. Schematic representation of a diverging beam passing through a Miche terferometer. The angle between the central ray and the extreme ray is α, and the distance moved by the mirror is *l*, corresponding to a nominal optical retardation the central ray.

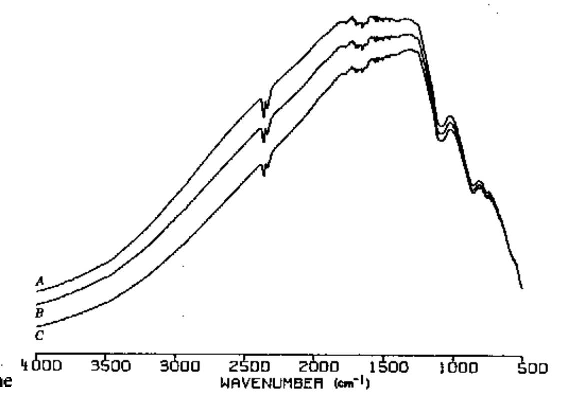
Diverging beams (tilt mirror or poor parallelism) lose intensity high wavenumber,

broaden spectra, and can shift wavenumbers – *must design in stability, smooth motion*

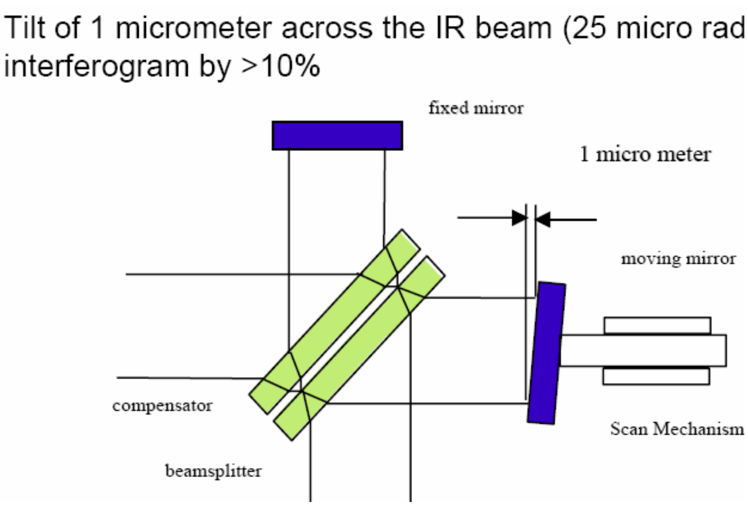
Similarly *mirror align* cause loss intensity, high wavenumber →(long λ favor FT IR application)

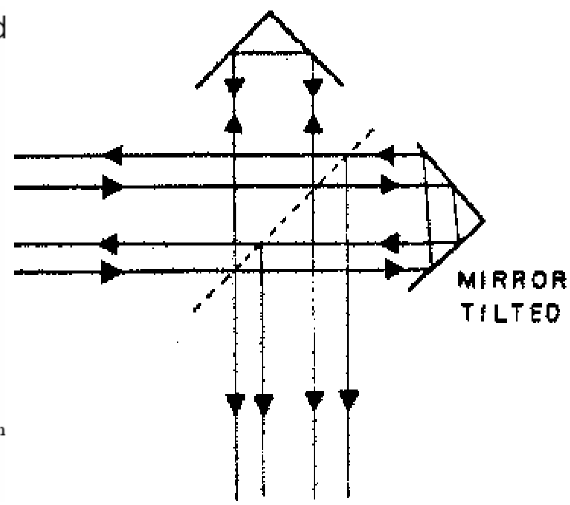


.22. Schematic representation to demonstrate the effect of changing the plane of the ıg mirror of an interferometer during a scan. Rays *A* and *B* represent the extreme rays : collimated beam passing through the interferometer, and β is the angle by which the of the moving mirror tilts.



ı. 1.23. Single-beam spectra measured (*A*) with the fixed mirror of the interferometer good alignment with the moving mirror, (*B*) with the fixed mirror slightly out of alignment, d (*C*) with the fixed mirror well out of alignment.





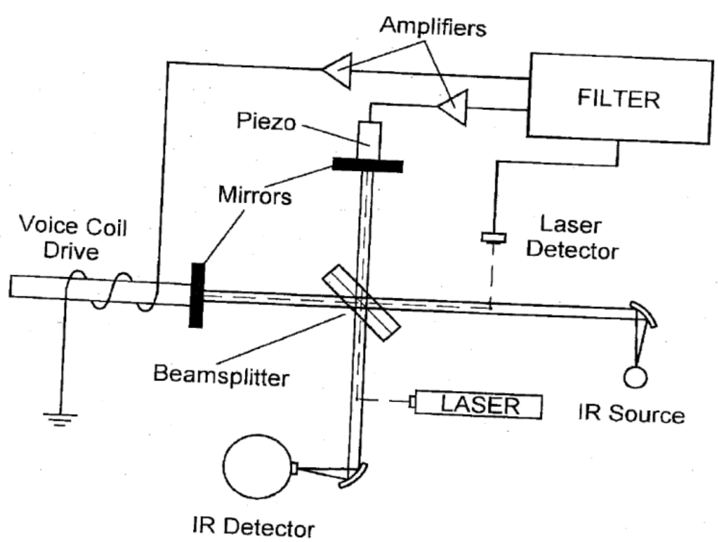
Simple correction (inexpensive designs) use *corner-cube mirrors*, self correct alignment

f. Indirect measure — need F.T. — computer must be fast, need *accurate co-addition* of scan

few people can interpret interferogram directly, so processing is vital step, even setup

Design issues (see at right):

Typically move mirror with a voice coil
pull-push drive shaft through magnet
Control position/speed with a HeNe laser
and Separate detector & BeamSplitter
Can adjust fixed mirror with Piezo
Dynamic Align (see below)
Motion of mirror stay smooth – parallel
Source must be collimated to parallel
beam at beam splitter – J-aperture
Detector typically small area, fast focus
Computer digitize signal, coadd, FT



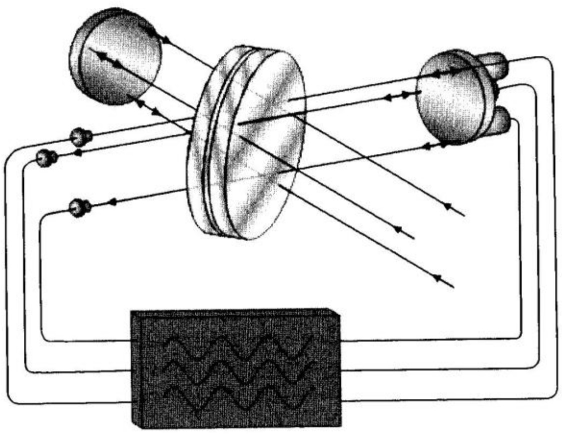


Figure 5.10. Path of three parallel laser beams through a dynamically aligned Michelson interferometer. The beams are detected by three separate detectors, and the signals from the detector are fed to three actuators that control the alignment of one of the mirrors. (Reproduced from [5], by permission of John Wiley & Sons, Ltd.; copyright © 2002.)

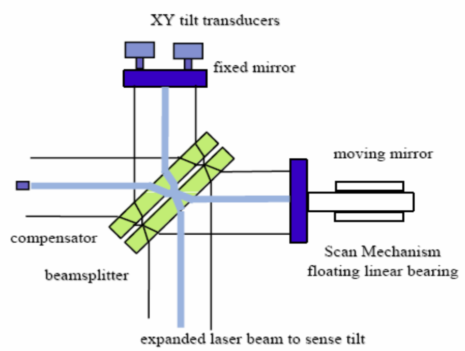
Dynamic alignment, get three laser signals in phase

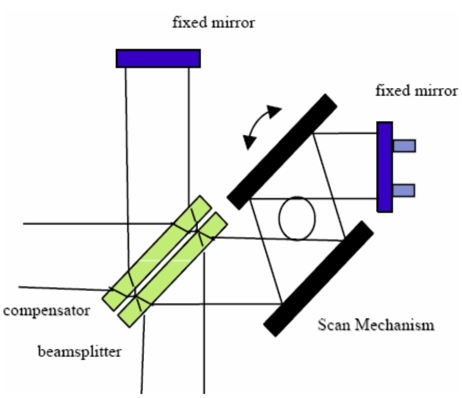
Following slides - borrowed from ABB Bomem – problem of mirror alignment

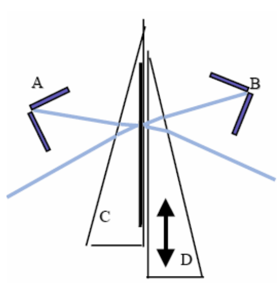
Dynamic alignment, adjust fixed mirror compensate for moving mirror

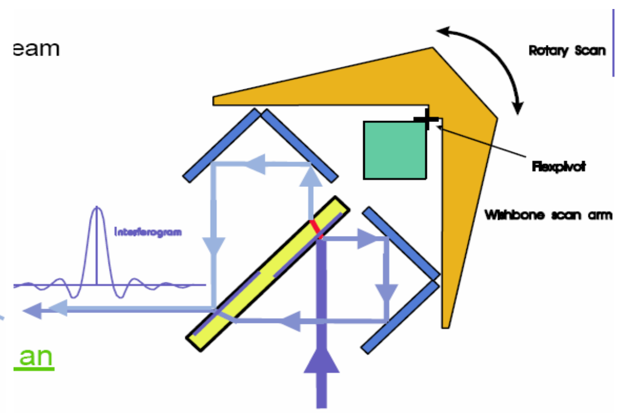
Advantages:
- stable
- simple interferometer optics
- repeatability is good

Disadvantages:
- dynamic tilt compensation shifts optical axis
- large central obscuration
- needs intitial and occassion realignment
- Reproducibility not controlled









Rotation keeps mirrors fixed

Path changes - Perkin-Elmer

sliding wedges same

corner cubes work most easily

Bomem wishbone pivot (other similar)

g. Survey of Drive systems (handouts)

1. classic 90° interferometer, - laser for tracking motion + “white light” interferometer to get initial starting position (high frequency-rapid oscillation, broad → single sharp center burst)

White light interferometer off-set, so mark occurs before IR interferometer (phasing)

Laser interferometer makes regular pattern of marks for triggering data collection

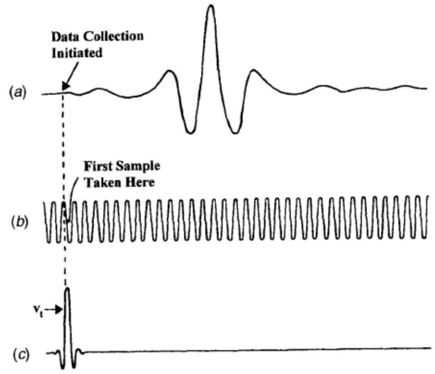


Figure 5.9. Interferograms measured using an interferometer of the type shown in Figure 5.8, showing the signals measured by (a) an infrared detector, (b) a laser detector, and (c) a white-light detector. Note that the reference interferometer is positioned so that the centerburst of the white-light interferogram occurs before that of the infrared interferogram. When the amplitude of the white-light interferogram exceeds the threshold voltage, V_t, data acquisition is initiated at the next zero crossing of the laser interferogram.

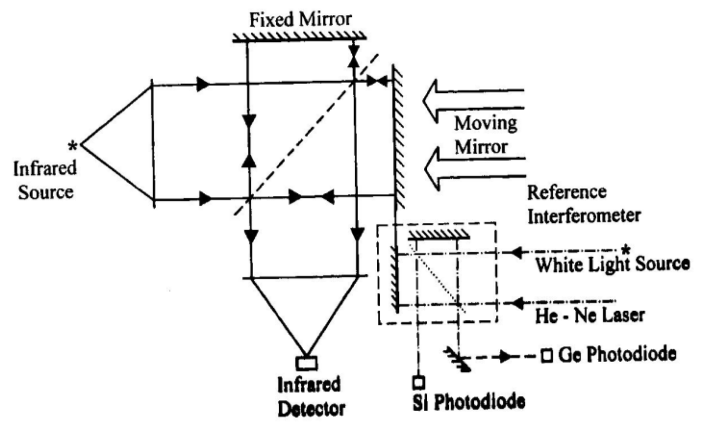
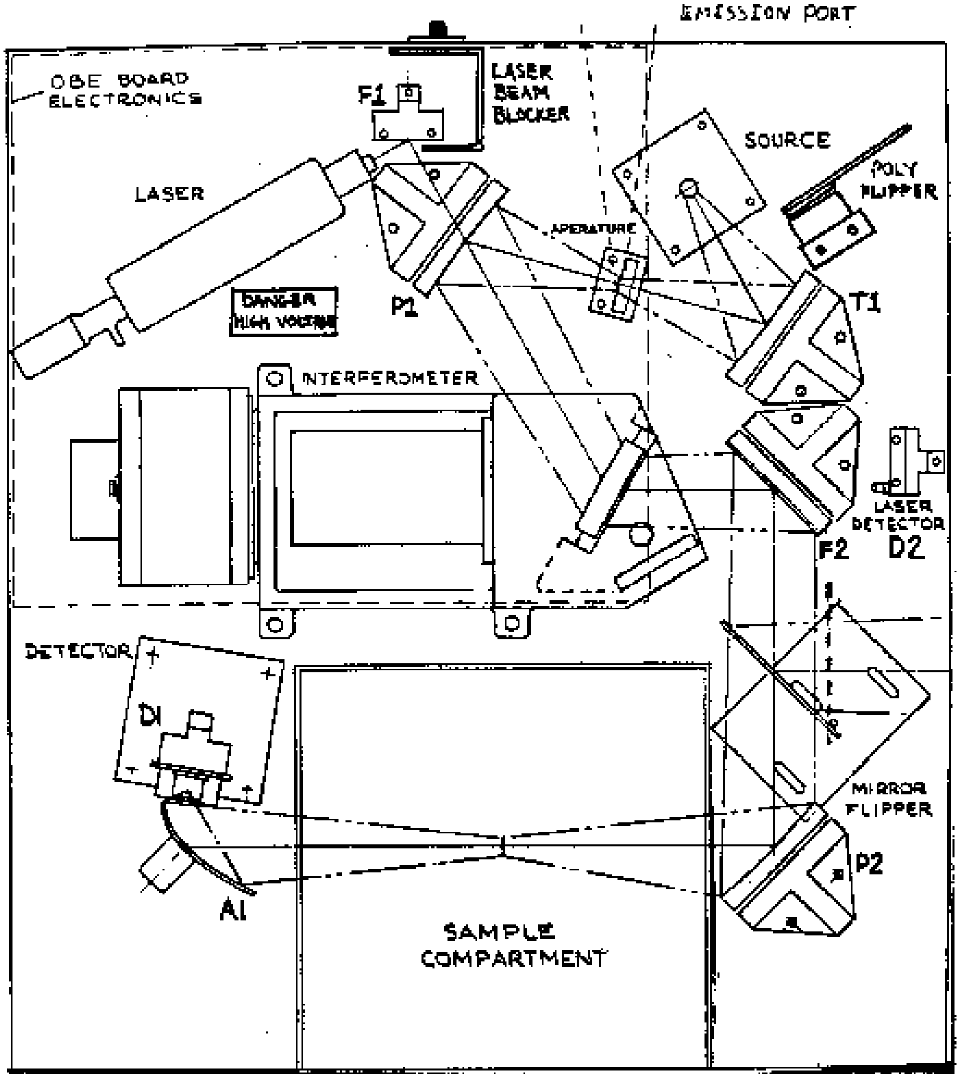


Figure 5.8. Interferometer, incorporating a separate reference interferometer for the laser and w

Used to be large installation, and had company specific computers, “big deal”, like some NMRs

then became more compact, bench top, used more normal computers, *fringe counting control*

2. Above pictures have bit more modern (20 years ago!) *compact design*, *no white light*, 60° interferometer, *HeNe laser interferometer* is clear aperture in center of beam splitter

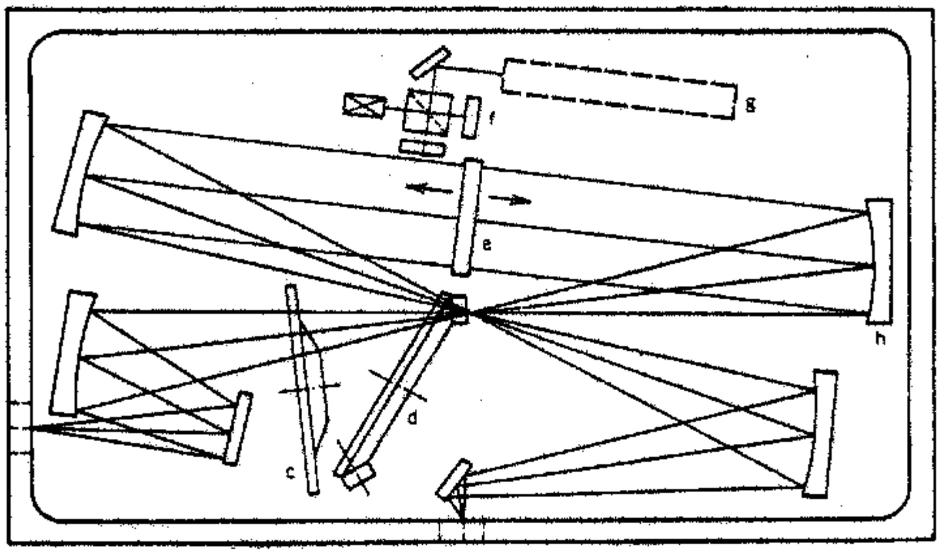


Mirror position determined by laser fringe counting, use frequency to stabilize mirror speed, laser reference gets wavenumber accuracy (limited by laser modes, but IR worse - aperture)

These spectrometers can get big. Bruker IFS 125 can have a resolution of < 0.001 cm^{-1} but this requires a path difference of ~ 10 m, but with folding can keep mirror motion inside the lab

Regular (whole lab version) "mobile" version has ~0.008 cm^{-1} res

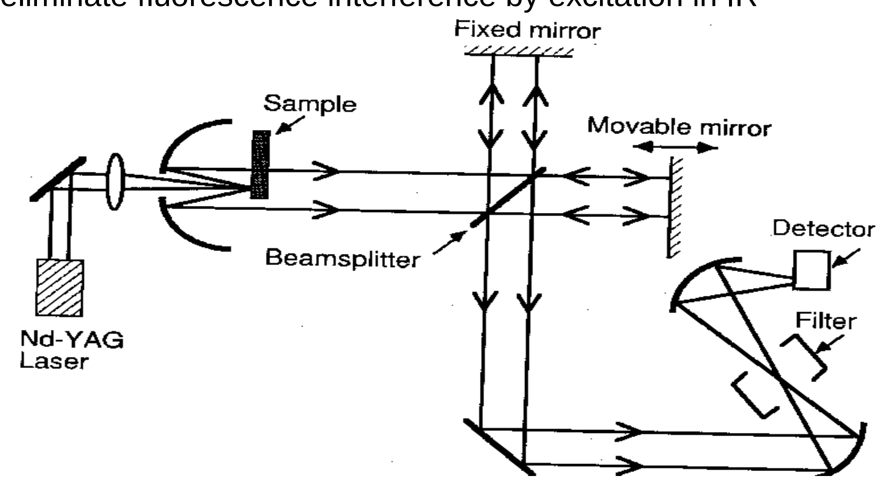
3. Genzel spectrometer, uses small *beam splitter at focus*, has several beam splitters on a wheel, choose without opening (*vacuum design—avoid need for flushing, eliminate water etc.*) Double sided mirror, so motion one arm is opposite for other arm, gives *retardation* **$\delta = 4\Delta x$**, need less motion for same resolution, laser interferometer is separate, but mechanically coupled to the mirror motion - (initial Bruker FTIR spectrometer)



Current models smaller, and cover range of applications, just like other FTIR companies

Alpha – tiny, routine analyses   Tensor – research lab FTIR   Vertex – higher res, flexibility

4. Application of *FT-Raman* spectrometer, use YAG laser to excite sample, collect scatter light, parallel detection with FT process, that is advantage, but lose with the detector compared to CCD and lose as $I_R \sim \nu^4$. Result is only real advantage is looking at messy samples and eliminate fluorescence interference by excitation in IR

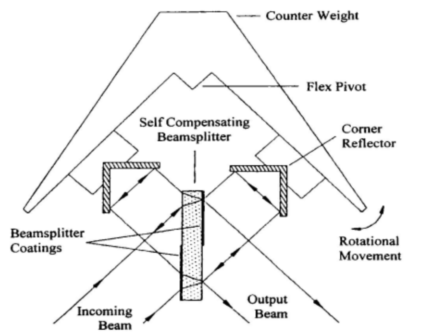


5. mini spectrometers now a big market issue (see also Alpha – Bruker above):

Bomem 3600 Thermo (Nicolet) S-10, variable sample chambers

JASCO compact, normal interferometer

Bit bigger yet compact, see inside at: http://www.mb3000ftir.com/html/quicktour.html



16. Double-pendulum interferometer of the type first described by Rippel and Jaacks BB-Bomem in their MB series instruments.

Even hand held and remote detection examples

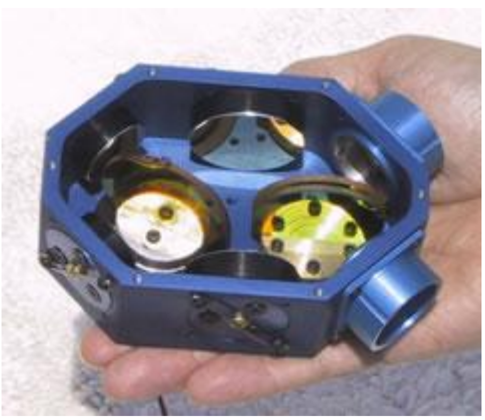
Bruker in a case, remote use on site

Thermo Ahura hand held First Defender – for untrained user

Jasco 9500, compact, attach different sample units

Interspectrum 9kg, 21x22 cm, ATR

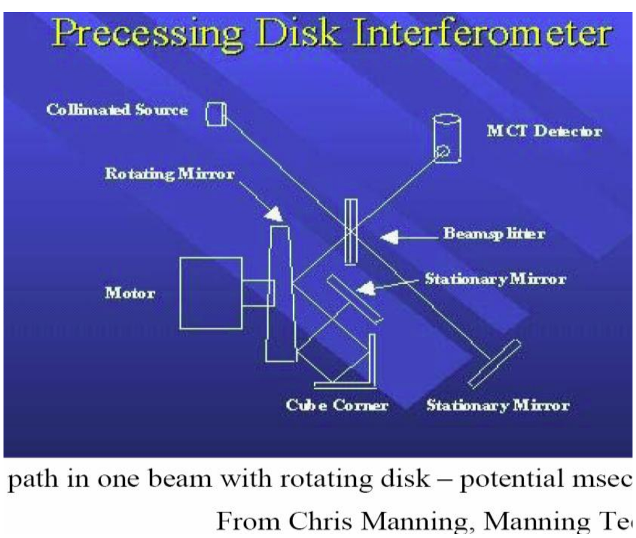
On the job use, dedicated analyzer

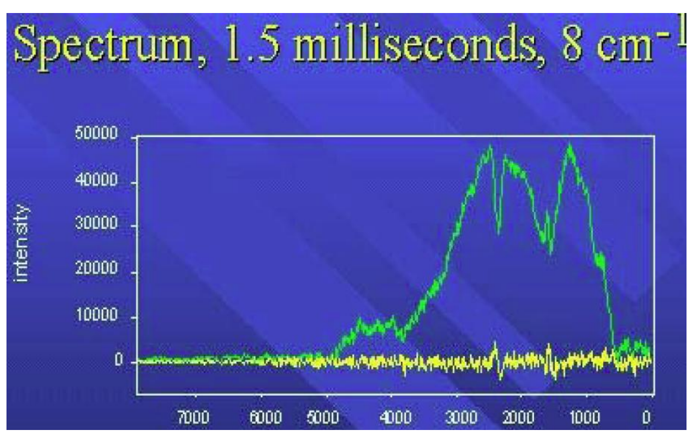


Micro is next goal (D&P Instruments)

Stand-off remote detection, especially gases

Very fast scanning, rotate mirror off axis, varies path





Go very fast: imagine kinetics studies

Homework—Sect 7 – part of homework #2

Reading as described at beginning of section, plus minimum *Chap 1, Griffiths and deHaseth*. Look at handouts and links

Discussion:

a. Consider experiments where an interferometer would be a better (or worse—goes both ways) choice than a monochromator, why?
b. The throughput advantage of an FTIR is always stated with regard to having no slit, but an FTIR has an aperture, and needs to make it smaller to increase resolution, why? How does this affect the Jacquinot advantage?
c. The Genzel interferometer gets retardation ~4Δx while "normal" interferometers, like classic Michelson, have retardation ~2Δx. How does retardation vary for the Bomem wishbone configuration interferometer, p.11 (Notes 7)? Why?

Problems to hand in: Chap 3 # 8, 23, 24,

a. I have an old FTIR that can get 0.5 cm^{-1} resolution with a design like that on p.13 (Notes 7). How far must the mirror move at minimum to get this resolution with an asymmetric scan (one sided interferogram)? What about for a symmetric (two-sided) interferogram? The maximum scan rate on this instrument is stated as 20 kHz, which is the frequency of modulation of the laser reference signal. Since this is a HeNe, 628 nm, how fast does the mirror move??
b. This original FTIR was upgraded with a new design, but now capable of 0.07 cm^{-1} resolution and 340 kHz scan speeds (laser modulation), how do your answers change for the upgrade (while a different design, 2Δx is still retardation)? At this resolution I cannot do a 2-sided interferogram using this design. Why not?
c. The Nyquist condition states that I need to sample a waveform at least twice every cycle (at $2 \cdot f$ in time, or $\lambda/4$ in Δx space) to properly digitize the variation in the signal. If I want to measure spectra over the range from 500-2000 cm^{-1}, how frequently must I measure the interferogram (Δx) – this is critical for step-scan experimental design – using a typical Michelson design ($\delta \sim 2\Delta x$)?

Links

Fabry Perot—

Wikipedia Fabry-Perot tutorial
http://en.wikipedia.org/wiki/Etalon
Drexel laser course on Fabry Perot:
http://repairfaq.ece.drexel.edu/sam/CORD/leot/course10_mod05/mod10-05.html

FTIR oriented sites, Michelson interferometers:

A variety of FTIR links, including sampling, companies, tutorials etc. from Michael Martin, Lawrence Berkeley Lab, ALS Beamline for IR work.
http://infrared.als.lbl.gov/FTIRinfo.html
Information about use of synchrotron for IR is here:
http://infrared.als.lbl.gov/viewgraphs/
Univ. Nantes set of instructional pages on Interferometers:
http://www.sciences.univ-nantes.fr/physique/enseignement/english/theoric.html

FTIR companies

Nicolet—Thermo now owns—range of products, emphasis on analytical lab
http://www.thermo.com/com/cda/category/category_lp/1,,234,00.html
Digilab—Varian purchased after BioRad and independence—research emphasis, early developer:
http://www.varianinc.com/cgi-bin/nav?products/spectr/ftir/index&cid=IIKJLOMMFN
Bruker—German company with wide range of instruments, including high res., time resolved, microscopy:
http://www.brukeroptics.com/ftir/index.html
ABB-Bomem—Canadian owned by ABB, has high res. and small rugged designs (process)
http://www.abb.com/analytical
MIDAC—compact rugged FTIR
http://www.midac.com/
Jasco—Japanese company -wide range of analytical spectroscopy instrum., including FTIR
http://www.jascoinc.com/products/s_ftir_raman.html
Perkin-Elmer – has long history in IR and analytical lab support
http://las.perkinelmer.com/Catalog/default.htm?CategoryID=FTIR+Systems
Many others—see LBL link above for many leading sites
http://infrared.als.lbl.gov/FTIRinfo.html