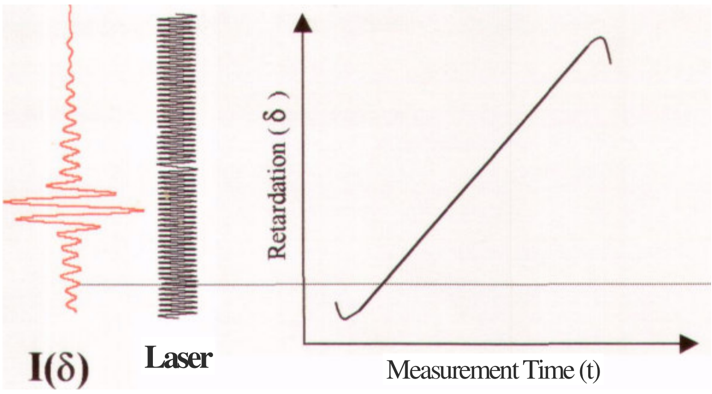
The interferogram is a function of the mirror position, only!

A. Linear (or Continuous) Scan Interferometry



In linear scan, the movable mirror is scanned at a *constant velocity,* u (cm/s), and the optical path difference at any time *t* is given by $\delta = 2ut$ (cm). The interferogram data point is digitized at the zero crossings of the HeNe laser signal on the fly. This mechanism ensures that $I(\delta)$ is measured at precisely equal intervals of mirror positions and provides an internal wavelength calibration for every scan ***(Cannes Advantage).*** *

In linear scan, the interferogram /(£) becomes an explicit function of time. The *(temporal} Fourier frequency* for IR light at wavenumber $\underline{v}$ is given by,

$$f_{\bar{v}} = 2uv \qquad (1)$$

The interferogram becomes time-dependent. Fourier (Modulation) frequencies depend on the wavelength of the IP light.

Linear scan works well for routine measurements on samples that do not change or change very slowly relative to the time needed to complete the measurement

* Modern FT-IR spectrometers use a *monochromatic* HeNe laser (15.798 cm"[1]) as an internal reference. Spectrometers monitor the HeNe laser signal constantly and whenever certain zero crossings (prc-defined and selected in the software) are detected, the digitizer is signaled to collect data points. This mechanism allows the interferogram to be collected at precisely equal intervals of mirror position.

(20 milliseconds for rapid scanning). For *lime-dependent processes* occurring on the same or faster time scales as the data collection time, linear scan is no longer useful. In this case *temporal Fourier frequencies* will interfere with the measurement of the *lime-dependence* of the process itself. The difficulties associated with linear scan can be overcome with step scan interferometry.

B. Step Scan Interferometry

In step scan, the movable mirror is moved *incrementally in steps.* This mechanism eliminates the time-dependence of the interferogram and temporal Fourier frequencies that are created by linear scan.

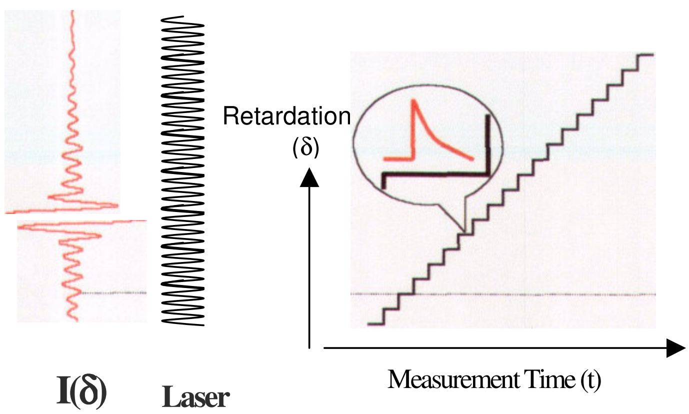
Temporal Fourier frequencies are eliminated in step scan!

Step scan experiments can be classified into two categories: *step scan with or without phase modulation* (PM) on the mirror. They are also referred to as the *time- OT frequency-domain* experiments sometimes. In the former, both mirrors are stopped completely when the data are collected at each mirror position while in the latter one of the mirrors is oscillated back and forth at a fixed frequency to modulate the IR light.

Examples of time-domain experiments include time-resolved spectroscopy (TRS) and amplitude modulation experiments where the data are collected with both mirrors stopped completely. Photoacoustic depth profiling and polymer stretching are examples of frequency-domain experiments that are conducted with PM on the mirror.

1. *Time-Domain Step Scan*

In a typical time-domain experiment such as TRS, the data are collected at each mirror position as an explicit function of time when both mirrors are stopped completely as shown in the figure below. The enlarged insert illustrates the time profile of the process under study. This time profile is recorded at each mirror position. The data are sorted into interferograms by

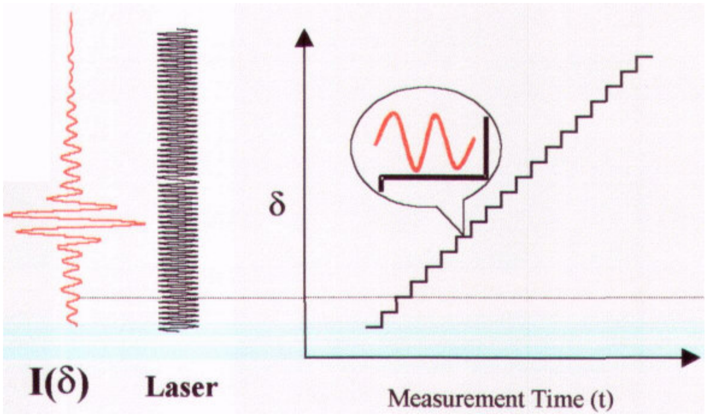


time that are then transformed to obtain the IR spectra at those times.

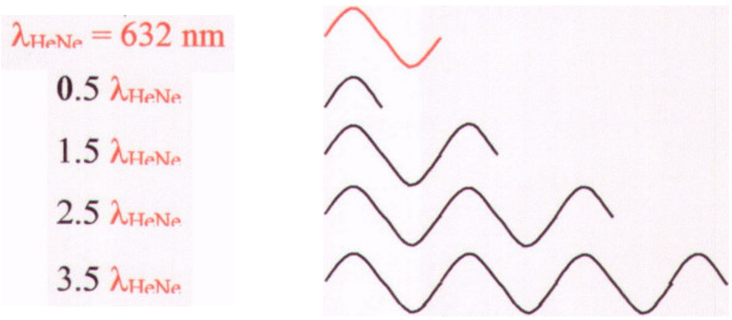
- *Step* scan TRS can measure repeatable, time-dependent processes that last 10 nanoseconds (ns) or longer.
- Mirror position must be maintained at very high precision to achieve good signal-to-noise ratio

2. *Phase Modulation Step Scan*

In a PM experiment, the movable mirror is moved to a position and then one of the mirrors is oscillated back and forth at a fixed frequency to modulate the IR light as illustrated below. Lock-in detection is normally used to demodulate the detector signal at PM frequency.



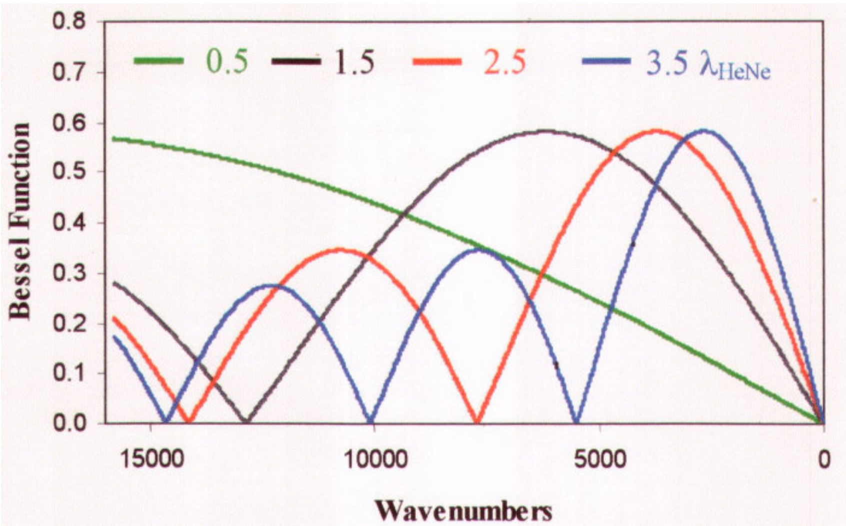
There are two important PM parameters: frequency and amplitude. The PM frequency (measured in Hz) refers to the number of mirror oscillations in a second. The PM amplitude measures the distance of the mirror oscillation and is usually expressed in terms of the HeNe laser wavelength (λ_{HeNe}) as illustrated below.



- All wavenumbers are modulated at the PM frequency.
- Modulation efficiency is wavelength-dependent.

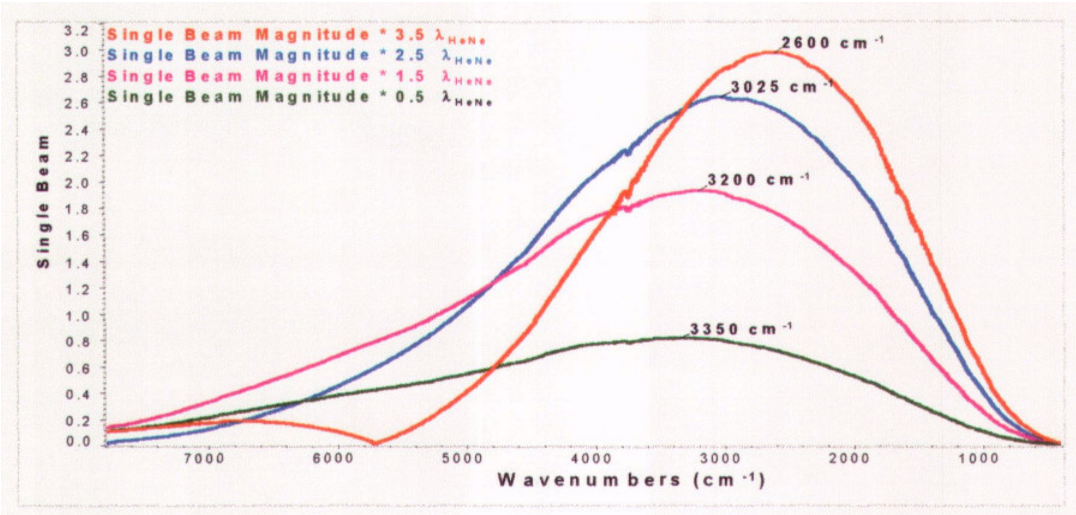
3. ***Phase Modulation Characteristics***

The PM modulation efficiency varies as a function of wavenumbers and modulation amplitude. For a given modulation amplitude, the wavenumber dependence is referred to as the phase modulation characteristics which can be described by first order Bessel function. The Phase modulation characteristics at PM amplitudes of 0.5, 1.5, 2.5, and 3.5 λ_{HeNe} are shown in the plot below.



All Bessel functions share the following characteristics: (1) ***The first lobe (from low energy) is the largest and the ones at higher energies become increasingly smaller in magnitude. (2) The lobes become narrower and shift to lower energies as the PM amplitude increases.***

The throughput of any experiments with phase modulation will include the phase modulation characteristics as illustrated below. Typical single beam spectra measured with a DTGS detector at PM frequency of 400 Hz and different amplitudes are shown in the figure below. The throughput in the finger print region is improved significantly from PM amplitude of 0.5 to 3.5 λ_{HeNe}. However, the throughput in the near IR region is lowered at PM amplitudes of 2.5 and 3.5 λ_{HeNe} because of the presence of nodes.



The PM amplitude should be chosen according to the spectral range of interest. PM amplitudes of 0.5 λ_{HeNe} or 1.5 λ_{HeNe} are appropriate for a near infrared experiment. The PM amplitude of 3.5 λ_{HeNe} provides an excellent coverage over the entire mid-IR region. Larger PM amplitudes will shift the largest lobe to lower energies and, at the same time, will bring nodes into mid-IR region.

The PM frequency should be selected based on the characteristics of the detector and other constraints of the experiment. For example, in polymer stretching experiment where multiple modulations are used, different frequencies should be separated by a factor of 10 or larger. For PAS depth profiling, PM frequencies are chosen according to the desired sampling depth.

CRITICAL FACTORS FOR STEP SCAN

Stability

Mirror position
PM Frequency
PM Amplitude