



VCD PART 1: FT OR DISPERSIVE?

Many more people than in the past are now talking of VCD (Vibrational Circular Dichroism), let's simply define it as the technique which allows to collect CD spectra in the IR range.

Today there is only one commercial VCD apparatus (the Chiral^{ir}™ by Bomem-BioTools), but at CD conference in Sendai Jasco exhibited an alternative preproduction unit which will probably have a future. Many leading FT/IR manufacturers (Bruker, Digilab, Jasco, Nicolet ...) are also offering CD accessories (not cheap) for standard FT/IR units.

For mid IR range all units make use of ZnSe PEM modulator (Hinds) and liquid N₂ cooled MCT detector.

From hardware side it's not such an easy job, since you add a second modulation (the PEM one) to the one built in by the interferometer moving mirror.

So in a few laboratories home made dispersive VCD unit are still in wide use.

Would you buy today an IR spectrophotometer still based on a conventional grating monochromator?

Probably not, even because it's now virtually impossible to find one, all leading IR manufacturers switched since years to FT interferometers only

Reasons behind are many, we all know a few of the FT advantages versus the dispersive approach, such as:

1 - multiplex (or Fellgett) advantage

FT/IR measure full spectra simultaneously, while dispersive systems measure one wavenumber after the other

This is a clear plus, same s/n can be achieved in much shorter time

2 - throughput (or Jacquinot) advantage

Source beam is fully used (at least at relatively low resolution when optical apertures can be avoided), while in dispersive systems most of the source emission is vignettted by the entrance slit

3 - wavenumber accuracy (or Connes) advantage

Interferometers have a built in HeNe laser source, so in theory wavenumber accuracy is as good as 0.01cm⁻¹

This is not fully correct since wavenumber accuracy will depend also/mainly from the number of data points (if you want resolution) used

4 - high resolution

In theory you can get easily more resolution increasing number of data points, i.e. the stroke of the moving mirror.

But in practical terms optical considerations still apply, since practical resolution will be limited by the parallelism of the beam in the interferometer, which can be improved only using narrow apertures spoiling the Jacquinot advantage.

At last we should add another advantage: with modern electronics FT/IR spectrometers are *cheaper* to build than conventional dispersive systems.

So going to VCD, since signal intensities are typically very low (lower than in electronic CD) it may seem that VCDs based on interferometer and Fourier Transform are the only *modern* choice.

But you'd consider that:

-to avoid saturation of MCT detector (and to remove other artifacts ...) optical filters are used in FT/IR VCD.

-the double modulation, at not so far spaced away frequencies, is a tasking job for the lock-in amplifier. (in UV-VIS CD you have no modulation apart from the PEM, in dispersive VCD you must modulate the beam since IR detectors do not operate properly in DC mode, but chopper frequency may be far away from the PEM one)

-FT/IR are making interferograms you convert by data processing into spectra, dispersive systems are making directly spectra; this seem a trivial point, but it makes some differences since in VCD signal intensity is typically very low and difficult to extract.

-For some specific applications (for example secondary structure estimation of proteins) the wavenumber range of interest is very limited for a single experiment, spoiling the multiplex advantage.

These facts explain why in a few leading laboratories dispersive VCD are still widely used.