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FAR–INFRARED FOURIER SPECTROSCOPY MADE PAINLESS

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THE method of interferometric Fourier transform spectroscopy (FTS) revolves around the fact that the interference pattern obtained from a two-beam interferometer as the path difference between the two beams is altered is the Fourier transform of the light illuminating the interferometer. This seemingly indirect technique has enjoyed spectacular success in the last decade, for routine far-infrared spectroscopy and in the more exotic field of infrared astronomy, due mainly to the ability of interferometric Fourier spectrometers to record all wavelengths of interest simultaneously. This leads to the so-called multiplex advantage. In energy-limited regions of the IR spectrum the low signal/noise obtainable by conventional spectroscopic methods is thereby increased to a level which allows good quality spectra to be recorded in a fast and routine manner. Other fringe benefits of interferometers include higher instrumental resolution capability and more compact imaging systems for higher optical throughput than are possible with conventional grating spectrometers.

These remarkable energy advantages have revolutionized far-infrared spectroscopy, making this energy-limited but highly interesting spectral region readily accessible for spectroscopic observations. Ten wavenumbers or less (wavelengths of $>$ 1 mm) and resolutions $\sim$0.1 cm^{-1} or better for gaseous samples can now be routinely recorded with some commercial Fourier spectrometers.

Despite this superiority and the subsequent fact that some 300 or more commercial far-infrared Fourier spectrometers have been sold on the world market since their inception in 1962, the FTS technique has not yet gained universal acceptance. Considerable controversy is still aroused among physical and chemical spectroscopists, generally on the basis that the instruments are too complicated to operate and do not give reliable results except in the most experienced hands. Grounds for such criticism have been provided by the fact that:

1) The success of the Fourier transform technique depends ultimately upon easy access to a digital computer, as the desired wavenumber-intensity spectrum is not directly recorded but must be mathematically unscrambled from an interferogram trace by an inverse Fourier transform computation. A dedicated, on-line computer is thus well-nigh essential, for a fast turn-around time in processing results.
2) The indirect nature of the method obstructs feedback between man and machine, which is so essential for the optimization of experimental conditions and for the quick correction of operational errors. Even with an on-line computer, some time can pass before errors are spotted.
3) Until recently, commercial FIR Fourier spectrometers were not sufficiently automatic for routine laboratory applications. For example, in order to exploit the full spectral range of a typical FIR interferometer, it is necessary to change beam splitters two or three times. This involves breaking the instrumental vacuum (FIR spectrometers must be evacuated or purged with a dry inert gas to eliminate atmospheric water vapor), demounting the old film, mounting the new one, perhaps re-aligning the interferometer optics and re-evacuating the instrument. This is naturally a finicky, undesirable, time-consuming process which often requires the care of highly professional personnel. Other problems have arisen from the unrestricted combinations of instrumental scanning parameters afforded by some commercial instruments.

With a variety of experimental conditions to satisfy – spectral range, resolution, interferogram sampling interval, interferogram scan speed, amplifier time constant etc. – it is hardly surprising that less-than-satisfactory results have been reported by inexperienced operators! It is with these inadequacies of existing interferometric Fourier transform systems in mind that the Polytec FIR 30 Far-Infrared Fourier Spectrometer was devised and introduced in October 1971, as an instrument for routine spectroscopy in the 10-1000 cm^{-1} spectral region. The first installation was in the laboratory of Prof. Ludwig Genzel at the Max Planck Institute for Solid State Physics, Stuttgart, West Germany; since that time a total of 8 have been installed in Germany and in the U.S.S.R.

The FIR 30 is shown in Fig. 1. As a unique laboratory far-IR Fourier spectrometer, the system may be envisaged as consisting of the following sub-systems:

A) A broad-band source of far-IR radiation to provide a comparative base for absorption and reflection measurements.
B) An interference modulator, in this case a slow scanning Michelson interferometer to create the necessary interferogram functions from the broad-band radiation source.
C) A sample chamber, in which transmission or reflection measurements can be made on solid, liquid and gaseous samples.
D) A far-IR detector and signal amplifying system for recording interferogram signals.

E) A digital data system hinged around a small built-in computer to process the interference data and output the far-IR spectra, either in single-beam or double-beam format.

The main features which set the FIR 30 instrument apart from other commercial Fourier spectrometers may be conveniently discussed with regard to these essential sub-systems.

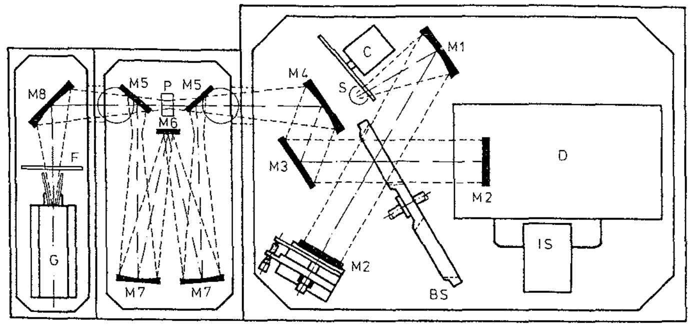
RADIATION SOURCE

An 80W high-pressure mercury lamp is employed as a far-IR source. This lamp operates with a dc arc and needs a high-voltage pulse to start the discharge. Lamps of this type tend to be more stable than ac lamps and are also more suitable at higher chopping speeds with faster detectors. When run at some harmonic of the line frequency, ac lamps could give additional unwanted modulation of the detector output. The chosen lamp is cooled by a closed loop water cooling system.

The properties of the high-pressure mercury arc lamp have been well documented and will not be discussed in detail here. It is worth commenting, however, that the radiative output arises from two sources: the hot (~ 3,500K) electron plasma within and the heated outer quartz mantle. At wavenumbers below 100 cm^{-1} the former effect predominates and at higher wavenumbers, nearly all the emission arises from the lamp jacket. For this reason, the radiative output of this type of lamp cannot be stabilized to a very high degree by electrical means, as the jacket temperature is affected by its vacuum environment, due to effects of convective cooling, etc. For high stability, therefore, constant vacuum conditions must be maintained around the lamp once a steady state running temperature has been achieved. This calls for a permanent uninterrupted vacuum in the interferometer chamber.

INTERFEROMETER AND CONTROL SYSTEM

The far-infrared vacuum Michelson interferometer is shown in Fig. 2. All-reflecting optics of approximately f/2 aperture and 65 mm nominal beam diameter provide a satisfactory compromise between the opposing desires for a high optical throughput and a modestly sized instrument.



M 1 Off-Axis paraboloid-collimator
M 2 Michelson-mirror
M 3 Plane mirror
M 4 Off-Axis paraboloid-condensor
M 5 Plane mirror (hinged)
M 6 Plane mirror
M 7 Spherical mirror
M 8 Toroidal mirror
C Chopper
S High Pressure Hg lamp
BS Beam splitter wheel
D Moving mirror carriage
IS Incremental measurement system
F Filter wheel
G Golay detector
P Sample

Fig. 2. Principal design features of FIR 30 vacuum Michelson interferometer system for the far-infrared. The interferometer, sample and detector chambers may all be separately evacuated.

Interferograms are recorded in a slow single scanning mode. The moving mirror displacement is clocked at regular intervals of 2.5 μm by a Moiré fringe system and the output pulses trigger the digital voltmeter, recording interferogram intensities. The maximum mirror travel is 10 cm, providing a maximum theoretical resolution of 0.05 cm^{-1} (the resolution is theoretically equal to the reciprocal of twice the maximum

TABLE 1 – OPERATIONAL PARAMETERS OF POLYTEC FIR 30 INTERFEROMETER

Instrumental Range Setting	Effective Wavenumber Range	Beam Splitter Thickness (μm)	Low-pass Filter Combination	Typical Interferogram Scan Conditions: Time Constant (s)	Interferogram Scan Speed (μm/s)	Sampling Interval (μm)	Maximum No. of Spectrum Points that can be calculated in "Real-Time"
1	100-700 (1000)*	2.5	black polyethylene	0.2	2.5	5	3000 Single Beam 1500 Double Beam
2	50-500	6	black polyethylene + 2 mm clear polyethylene	0.5	5.0	5	3000 Single Beam 1500 Double Beam
3	20-180	15	black polyethylene + 3 mm Teflon	0.5	10	10	3000 Single Beam 1500 Double Beam
4	10-55	50	black polyethylene + 2 mm crystal quartz	1.0	20	20	3000 Single Beam 1500 Double Beam

*When polyethylene sample chamber windows are demounted mirror displacement from the zero path point in the interferogram). The advantage of a slow single scanning mirror drive system is its utilization of real-time Fourier transformation. A single scan also permits working over very large optical path differences. By contrast repetitive scan type interferometers are usually restricted to only one or two cm mirror displacement and hence to only moderate resolution.

Further distinguishing the FIR 30 are its optics. The interferometer does not employ the classical Michelson 45° incidence configuration but operates at 30° incidence to the beam splitter film. This is to reduce strong polarization effects due to reflection at the beam splitter surface. The Brewster angle for the Mylar beam splitter material is approximately 57°; the optical beam at the interferometer output is therefore predominantly polarized with the electric vector vertically, in the plane of the beam splitter. For example, in the 10-500 cm^{-1} spectral region, a 45° incidence Michelson interferometer usually has a 3:1 ratio of vertical:horizontal polarizations, whereas the 30° incidence configuration of the FIR 30 has been found to reduce this figure to 1.7:1. Good homogeneity of beam polarization is extremely important when polarized transmission and reflection studies are to be made on anisotropic materials at various orientations of the beam electric vector, and sufficient beam energy must be maintained in the reference beam for all cases.

This automatic beam splitter changer is a unique feature of the FIR 30. Any one of four beam splitters mounted on a wheel may be correctly positioned in the beam on external command. The rotating mechanism is so precise ($\lessdot$1 arc second out of plane deviation in 360° revolution) that the interferometer effectively remains in perfect alignment for all 4 positions, thus making the operation of changing a beam splitter a matter of turning a control knob and waiting a few seconds, instead of the usual half-hour-long procedure. Operating in tandem with the beam splitter wheel is a wheel carrying 4 low-pass filters positioned before the detector. The low-pass filters complement the band-pass transmission characteristics of the beam splitter films which have been chosen to optimize the energy over different portions of the instrument's operating range (see Table 1).

As Fig. 3 illustrates, scanning parameters such as mirror drive speed, time constant and interferogram sampling interval are automatically selected with the electrical spectral range selector (which itself controls the beam splitter and filter mechanisms). Thus, scanning parameters for a given spectral range are always optimized, reducing operator tasks to a minimum. For unusual studies, however, all the automatic controls may be overridden and set at other values, allowing full flexibility for research purposes.

SAMPLE CHAMBER

For great convenience, the sample chamber can be separately evacuated from the interferometer and detector chambers which are isolated by polyethylene or "TPX" windows. The approximately f/3 converging beam from the interferometer chamber is brought to a focus of about 12 mm ϕ in the center of the sample chamber; this is a convenient image size and geometry for most spectroscopic samples.

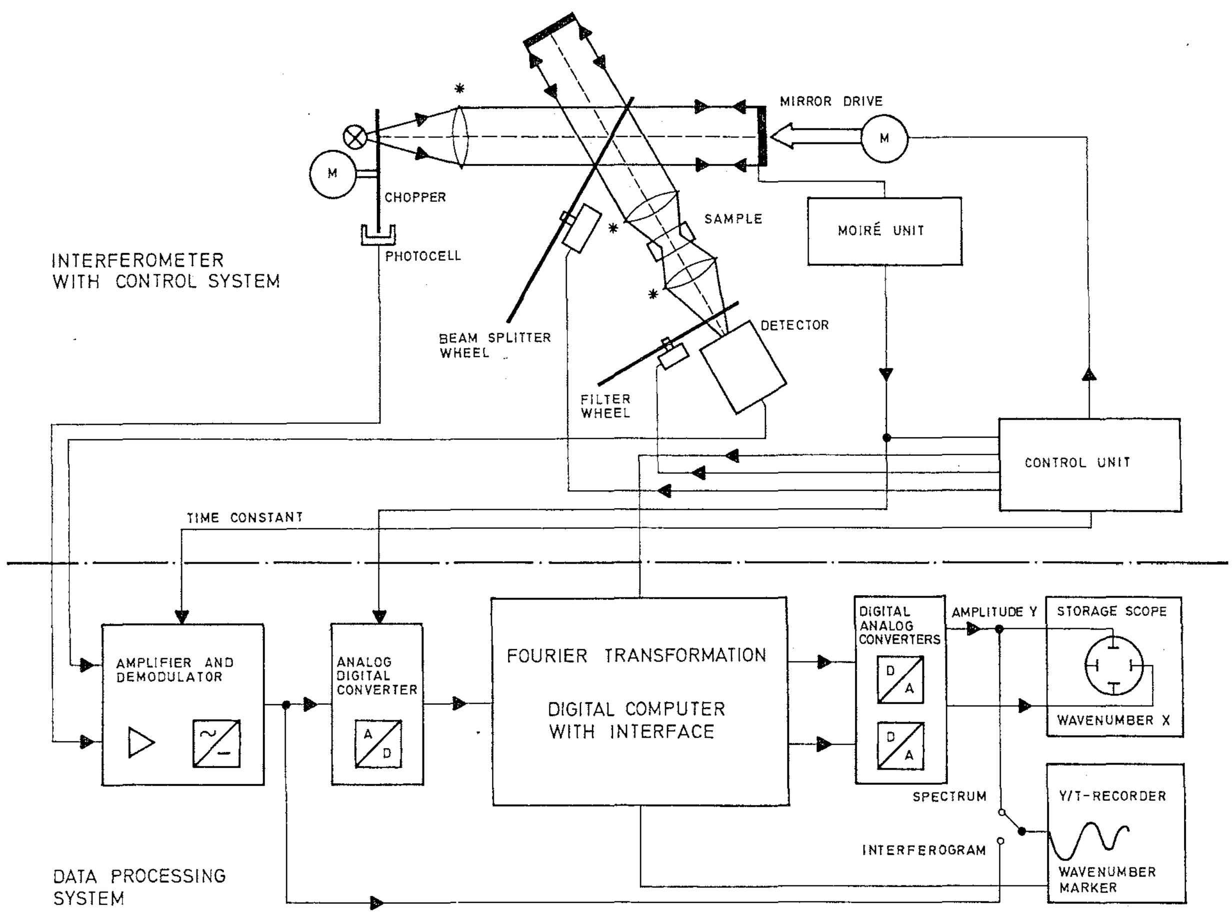


Fig. 3. Block diagram of FIR 30 electronic control and data processing systems (teletype terminal is not shown). For simplicity, lens-type optics have been drawn in for the interferometer.

Transmission and reflection measurement configurations are indicated in Fig. 4. The beam can be electrically switched between reflection and transmission by means of two small hinged plane mirrors. The availability of two effectively equivalent optical paths provides for the measurement of a sample (whether in transmission or reflection) and a reference spectrum without having to break the sample chamber vacuum. By replacing the plane reflecting sample with a spherical mirror, a White-type variable multi-pass gas cell configuration with up to 5 meters absorbing path is achieved.

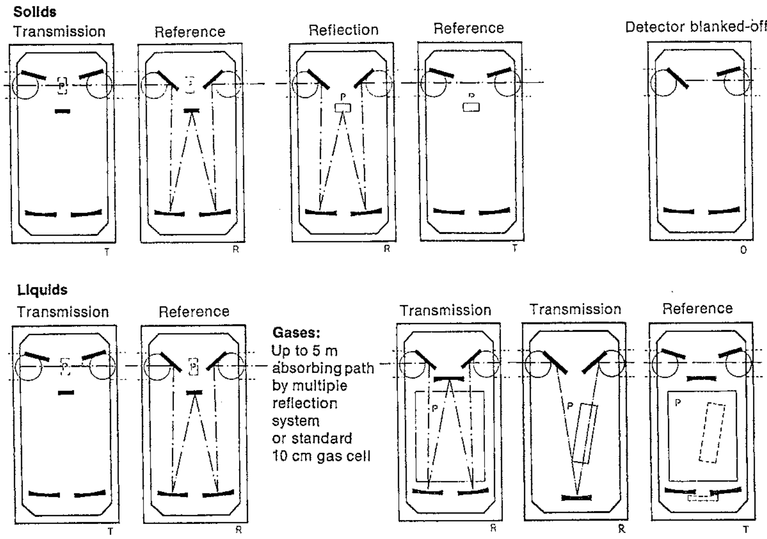


Fig. 4. FIR 30 Sample Chamber Optics. The beam is switched by means of externally controlled hinged mirrors.

In the reflection configuration, the optical beam is brought to no less than three focuses. An adjustable iris diaphragm may be inserted at the first focus to limit the image size at the second focus where the beam is to be reflected. This is very important when precise reflectance measurements on very small samples are required. In addition, far-IR wire-grid polarizers may be inserted at the first and third focus positions to allow the beam electric vector to be set at any required orientation with respect to the sample crystalline axes.

Reflecting samples of up to 12 mm ϕ are placed at the second focus position. The angle of incidence made by the optical beam center ray is about 11.5° at this position. This angle may be varied $\pm 2-3^\circ$ by adjusting the lateral separation of the two concave spherical reflectors. The sample chamber can be adapted to a variety of optical cells for solids, liquids and gases, at operating temperatures above and well below room temperature. A wheel-type sample changer has also been developed which allows 8 solid samples of up to 25 mmϕ or 4 liquid cells to be positioned in the beam without breaking the sample chamber vacuum. This saves much time and leads to better reproducibility of results.

DETECTION ELECTRONICS

The FIR 30 interferometer is readily adaptable to all types of far-infrared detectors, typical examples of which are listed in Table 2. For maximum convenience however, a room temperature pneumatic Golay detector (Pye Unicam IR 50) is standard. The IR 50 detector exhibits uniform spectral response over the entire far-IR region, has a high responsivity and shows negligible long-term drift in its output due to the utilization of all-solid-state opto-electronic components to minimize heat dissipation. Over the last 5 years both the IR 50 and its predecessor the SP 50 have been found to be relatively robust, free from microphony and have a good operating life (>3 years) as evidenced by their successful incorporation in a wide range of commercial instruments. Golay detectors of other manufacture, however, are reputed to be extremely fragile and unreliable and have given this type of detector an undeserved stigma, particularly in the U.S.A., where less sensitive TGS type pyroelectric bolometers have gained popularity. As Table 2 shows, TGS detectors have quoted noise equivalent power (NEP) values almost an order of magnitude greater than that of the Golay cell and are clearly inferior for far-IR spectroscopy when compared to the IR 50 detector.

The Golay cell has another property that is extremely important for Fourier spectroscopy; a high degree of linearity in its output over a wide dynamic range of optical input signals. A non-linear detector could produce not only absolute intensity errors but harmful distortions in spectra computed for a large number of spectral elements (the degree of linearity demanded of the detector-amplifier-digitizer chain of a Fourier spectrometer may be likened to that demanded of a good audio hi-fi system).

The liquid helium cooled Si and Ge bolometers listed in Table 2 exhibit considerably lower NEP than the Golay detector but are inherently non-linear (5% or greater) in their outputs due to their non-linear resistance-temperature characteristics. As the bolometer elements usually need to be shielded from room temperature radiation by various cold filters, their most useful range of operation is normally restricted to the 5 - 250 cm^{-1} spectral region. The need for a liquid helium cooled bolometer thus arises only where NEP is of paramount importance, such as high resolution studies of opaque materials at very low wavenumbers; these are generally of interest to solid state physicists. The various spectra presented here confirm that the IR 50 Golay detector has sufficient detectivity to meet the needs of routine far-IR spectroscopy with the FIR 30. Spectral resolutions as high as 0.1 cm^{-1} can be obtained and frequencies as low as 10 cm^{-1} can be recorded in moderate scanning times.

The FIR 30 electronics control and data handling system is shown in Fig. 3. The modulated detector output at 12-15 Hz (or higher frequencies in the case of faster detectors) is amplified, synchronously rectified and smoothed to give a dc signal proportional to the optical interferogram signal. On command of trigger pulses from the Moiré fringe counting system, the dc signal is digitized by a bi-polar 13-bit A/D converter, and the values transferred via a suitable interface to a 4K memory digital computer (Data General Corp. NOVA 1200), where they are processed in real-time.

REAL-TIME FOURIER TRANSFORMATION

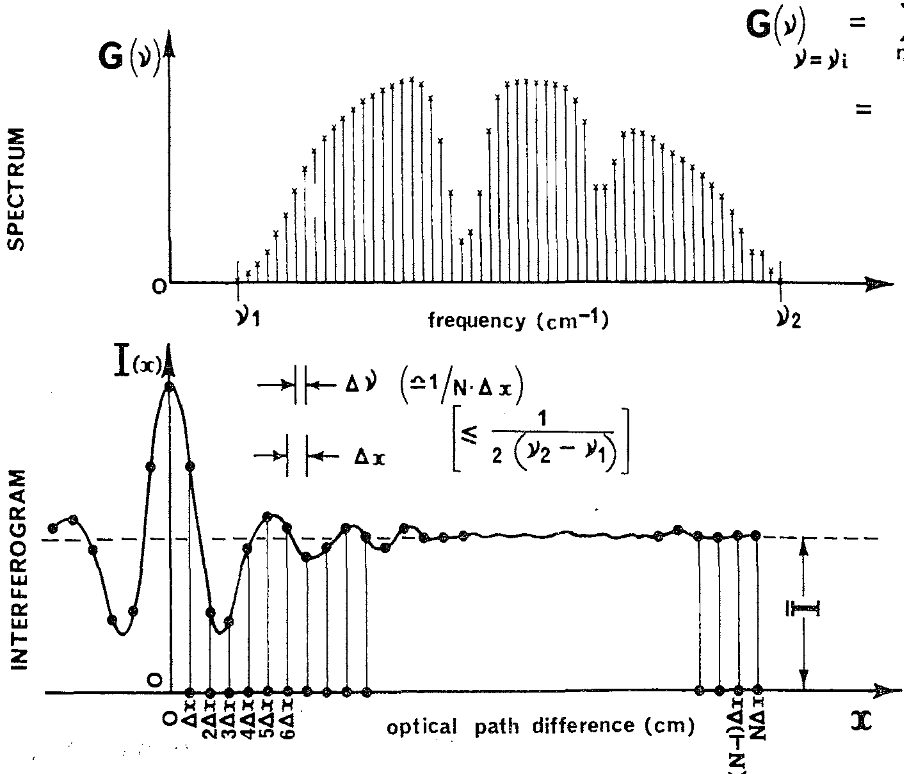
In order to discuss the problem of data processing, it will be necessary to recall the simplest basic mathematics of practical Fourier transform spectroscopy, as outlined in Fig. 5. To obtain the optical intensity G (ν_i) at any wavenumber ν_i using the cosine Fourier transform it is necessary to sum up all the Fourier terms computed from a regularly sampled interferogram function, starting at the position of zero optical path difference.

While in principle the spectrum can be calculated for any arbitrary wavenumber value ν_i the operator cares to inject in the calculation, the intensity values are normally computed for a regular array of wavenumber values which effectively straddle the spectral range of interest at a spacing compatible

TABLE 2 – COMPARISON OF SOME CURRENTLY AVAILABLE COMMERCIAL FAR-IR DETECTORS

Detector	Operating Temperature (°K)	Sensitive Area (mm²)	Normal Chopping Frequency (Hz)	NEP For 1 Hz Bandwidth (W)	Responsivity (V/W)	Detector Response Time (msec)	Deviation from Linearity	Operating range and other remarks
IR 50 Golay (Pye Unicam)	300	7 or 20 standard	10-15	1.3×10^{-10}	6×10^{5}	~15	<1% for input signals less than 3×10^{-6} W	5 to 1800 cm^{-1} with Type II Diamond window. All solid state electronics give good stability through low heat dissipation
Golay (Eppley Labs)	300	4.5	10-15	8×10^{-11}	10^{5}	~15	<1% for input signals less than 10^{-6} W	operating range as above. Generally reputed to suffer from microphony and short operating life
Type F363 TGS Pryoelectric Bolometer (Mullard)	300	3	10-1000	1.5×10^{-9}	1×10^{3}	~1	not stated	5 to 700 cm^{-1} with polyethylene window. Is of robust construction
Type Si 1.4R Silicon Bolometer (Molectron Corp.)	1.4	25	10-1000	6×10^{-14}	3×10^{5}	0.3	not stated	5 to 200 cm^{-1} with standard quartz filter. Fast and sensitive but is inherently non-linear for high incident signals
Germanium Bolometer (Texas Instruments)	2.2	15	10-1000	5×10^{-13}	4×10^{3}	0.4	not stated	5 to 500 cm^{-1} with suitable window/filter. Also inherently non-linear for high incident signals
Hot-Electron, Weak-Magnetic field type InSb Photo Detector (Mullard)	1.8	4	10-1000	5×10^{-12} at 10 cm^{-1} to 10^{-11} at 50 cm^{-1}	10^{3} at 10 cm^{-1} 2×10^{2} at 50 cm^{-1}	2×10^{-4}	not stated	Restricted to range 5 to 50 cm^{-1}

The NEP, a measure of the detector sensitivity is defined as the incident power which makes the signal/noise equal to 1 for a 1 Hz bandwidth.



$$
\begin{aligned}
G(\nu)_{\nu=\nu_i} &= \sum_{n=0}^{n=N}\left[I(n\cdot\Delta x)-\bar{I}\right]\cdot\cos\left(2\pi\,\nu_i\cdot n\,\Delta x\right)\cdot\Delta x\\
&= \left[I(0)-\bar{I}\right]\cdot\Delta x\\
&\quad+\left[I(\Delta x)-\bar{I}\right]\cdot\cos\left(2\pi\,\nu_i\cdot\Delta x\right)\cdot\Delta x\\
&\quad+\left[I(2\Delta x)-\bar{I}\right]\cdot\cos\left(2\pi\,\nu_i\cdot 2\Delta x\right)\cdot\Delta x\\
&\quad+\cdots\\
&\quad+\left[I(N\cdot\Delta x)-\bar{I}\right]\cdot\cos\left(2\pi\,\nu_i\cdot N\cdot\Delta x\right)\cdot\Delta x
\end{aligned}
$$

Fig. 5. Computation of spectrum from a regularly sampled single-sided interferogram function by cosine Fourier transform. The interferogram sampling interval Δx is limited by the band width $(\nu_2 - \nu_1)$ of optical frequencies received by the detector. The spectral resolution $\Delta\nu$ is inversely proportional to the length of interferogram trace. The cosine Fourier transform method demands the exact coincidence of an interferogram point with the zero optical path difference position. In the FIR 30 interferometer, the mean signal level $\bar{I}$ is subtracted electrically before computations commence.

with the optical resolution required. The Fourier transform computations thus take the overall form of a double summation of Fourier terms over interferogram points and over wavenumber points. This offers the possibility of two equivalent but non-identical methods of computing spectra, according to the order in which this double summation is carried out:

a) The complete set of interferogram data points is used to calculate intensity values for each wavenumber value, in turn (i.e., the summation is first carried out over interferogram points). This, to date, has been the conventionally accepted method of performing FIR Fourier transform computations on large digital computers, and also with the majority of commercial instruments incorporating built-in computers. In such cases, the Cooley-Tukey fast Fourier transform algorithm is normally incorporated in the computer program to cut computing time to a minimum.

b) Starting at the position of zero optical path difference in the interferogram, the Fourier terms are calculated for the selected array of wavenumbers from each individual interferogram data point in turn (i.e., the summation is first carried out over spectrum points). Each set of intensity values is stored and updated by the accumulation of corresponding Fourier terms computed from subsequent interferogram points.

While both methods give exactly the same result in the end, Method b) is particularly advantageous for far-IR Fourier spectroscopy. Firstly, the entire spectrum of interest is being continually evolved and can be observed at any stage of the interferogram scan (see Fig. 6), which is the essence of the so-called real-time method of Fourier transformation. In Method a), the whole interferogram scan must be completed before spectrum computations can commence. (For a high resolution spectrum this could involve a 1 hour wait). Secondly, only computed spectrum points need be stored in the computer memory, and not interferogram points, which are computed on the fly. It is thus possible with a relatively small memory digital computer to process a large number of spectrum points, from an unlimited number of interferogram points. In Method a), space must also be found for interferogram points as well as spectrum points in the computer memory, which for a given size memory effectively halves the number of interferogram or spectrum points that can be processed. Here the overall instrumental resolution becomes severely limited by the size of computer memory.

In the Polytec FIR 30, the standard 4K-16 bit word memory NOVA 1200 computer has been programmed for real-time operation, and may process up to 3000 spectrum points. Normally these 3000 locations are reserved, 1500 points each for a reference spectrum and a sample spectrum, to allow absolute double-beam transmission and reflection spectra of 1500 points to be measured. All calculations are carried out with 32-bit precision, which reduces residual effects of round-off errors in the computation to a level at least two orders of magnitude smaller than the typical ~1% noise content in a spectrum.

The speed of calculation is important, as the real-time computer must always be faster than the interferometer data accumulation rate. In the system described here, the time of calculation is linearly proportional to the number of output points and for 1500 spectrum points is ~0.4 seconds, well within the typical data rate of one interferogram point/second.

In a typical procedure for Fourier transform computations with the FIR 30 one first specifies (via the teletype unit) the experimental parameters to the computer as:

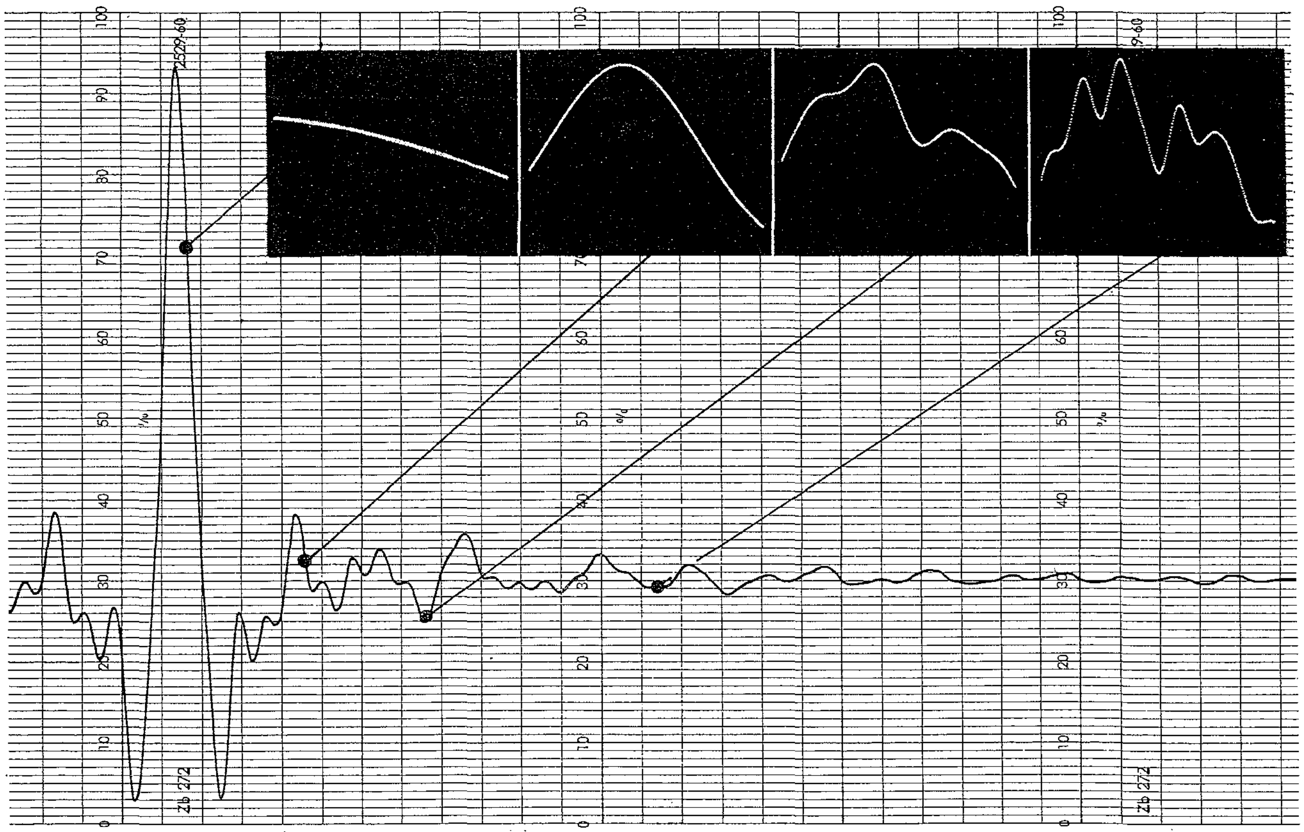


Fig. 6. Real-time spectrum displays observed on oscilloscope screen showing the build-up of spectral information as an interferogram scan progresses. The spectrum shows the absorption features of polypropylene in the range 80-430 cm^{-1}. The last picture was obtained after 1 minute scanning time and shows a resolution of 20 cm^{-1}.

– the lowest wavenumber value to be calculated
– the interval between calculated wavenumber values ($0.05\ cm^{-1}$ minimum unit)
– the total number of points in the spectrum
– the interferogram sampling interval
– the total number of interferogram points
– whether or not the raw data is to be apodized.

Having given this spectral information, one now indicates whether a reference or sample spectrum is to be calculated, by means of a 3-letter sequence command on the teletype, as illustrated in Fig. 7.

When the interferometer drive has been set in motion, the spectrum computations commence. The computer automatically seeks out the highest interferogram value recorded, and washes out all preceding calculations. In this way, the true spectrum computations always begin at the zero path interferogram summit. As shown in Fig. 6, the updated spectrum is displayed after each new interferogram point. An external selector allows bright wavenumber marker points to be superimposed on the screen at predetermined wavenumber intervals, as an aid to reading off the wavenumber axis. The calculations may be stopped manually whenever the spectral detail has ripened satisfactorily, or the computer can run out to the predetermined number of interferogram points.

As illustrated in Fig. 7, the stored spectral data may then, on demand, be re-displayed on the oscilloscope screen, plotted out on a chart recorder complete with wavenumber markings, or outputted on punched paper tape by the teletype unit. The rate at which the spectra are plotted out depends upon the sharpness of the spectrum and the recorder response time, but falls in the range 2-10 frequency points/sec. A particularly useful feature of the system is that interferogram data can be punched on tape during real-time operation so that a permanent record of the interferogram trace is obtained. The punched tapes may be read into the computer later, and new spectra can be calculated from this raw data.

An important feature of the FIR 30 real-time Fourier transform program is a routine for the correction of phase errors in recorded interferograms. Such errors can arise from the non-coincidence of an interferogram point with the interferogram summit at zero optical path difference. For the cosine Fourier transform these errors can cause both distortions of the spectrum baseline and of the instrumental resolution function, which become exceedingly pronounced at higher wavenumbers. In the FIR 30 interferometer, any such phase errors are first manually set to a minimum ($< \Delta x/10$, the worst possible case is $\Delta x/2$) by means of a very fine translational adjustment of the fixed Michelson mirror. Any residual errors are then computed from a theoretical parabola fit to the highest three sampled points on the summit; the interferogram optical path difference values and zero path intensity value are then corrected accordingly. In this way, any residual effects of phase errors can be kept below the typical noise level in broad-band spectra which usually amounts to 1-2% full scale.

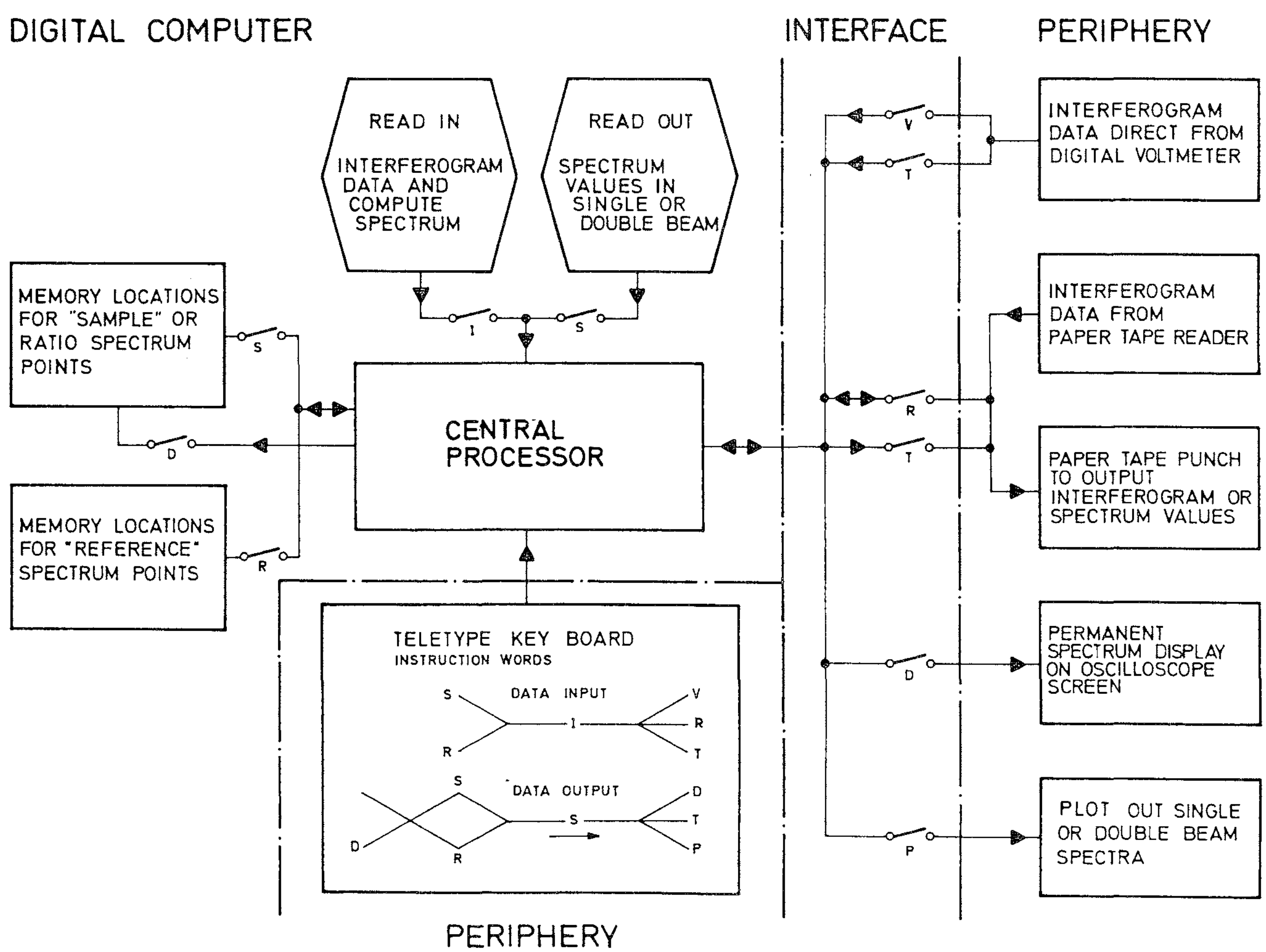


Fig. 7. Block diagram of FIR 30 digital data system. Three-letter commands typed on the teletype terminal control the flow of interferogram input or output data between peripheral systems and the main processor, and also spectrum output data.

PERFORMANCE AND APPLICATIONS

The ultimate test of any IR spectrometer is what quality of spectrum may be recorded and how long it takes to do so, in a certain wavenumber range at a certain resolution and with a certain type of sample. The basic rules of conventional infrared spectrometers also apply to Fourier spectrometers, i.e., that spectral resolution is finally dictated by signal/noise considerations and that the product (resolution) x (intensity accuracy) remains constant. Consequently, the highest spectral resolution can be obtained only for the most transparent media such as gaseous samples. In a similar fashion, the lowest wavenumbers obtainable are dictated by signal/noise considerations (between 20 cm^{-1} and 3 cm^{-1}, the mercury lamp radiative output drops two orders of magnitude in intensity).

Typical of the FIR 30 performance, Figs. 8 and 9 show two high resolution gaseous spectra recorded in very moderate scanning times. The two water vapor spectra in Fig. 8 illustrate the need for careful control of vapor pressure if high resolution features such as the 0.15 cm^{-1} doublet at 96 cm^{-1} are to be observed. The noise level of the two spectra may be judged from the intensity variations in regions of no known H_2O lines and may be estimated as ~5% full scale. The acetonitrile pure rotational spectrum shown in Fig. 9 was recorded in the difficult very low wavenumber region. The CH_3CN pure rotational lines of spacing 0.6 cm^{-1}, although showing some effects of broadening, have been clearly resolved.

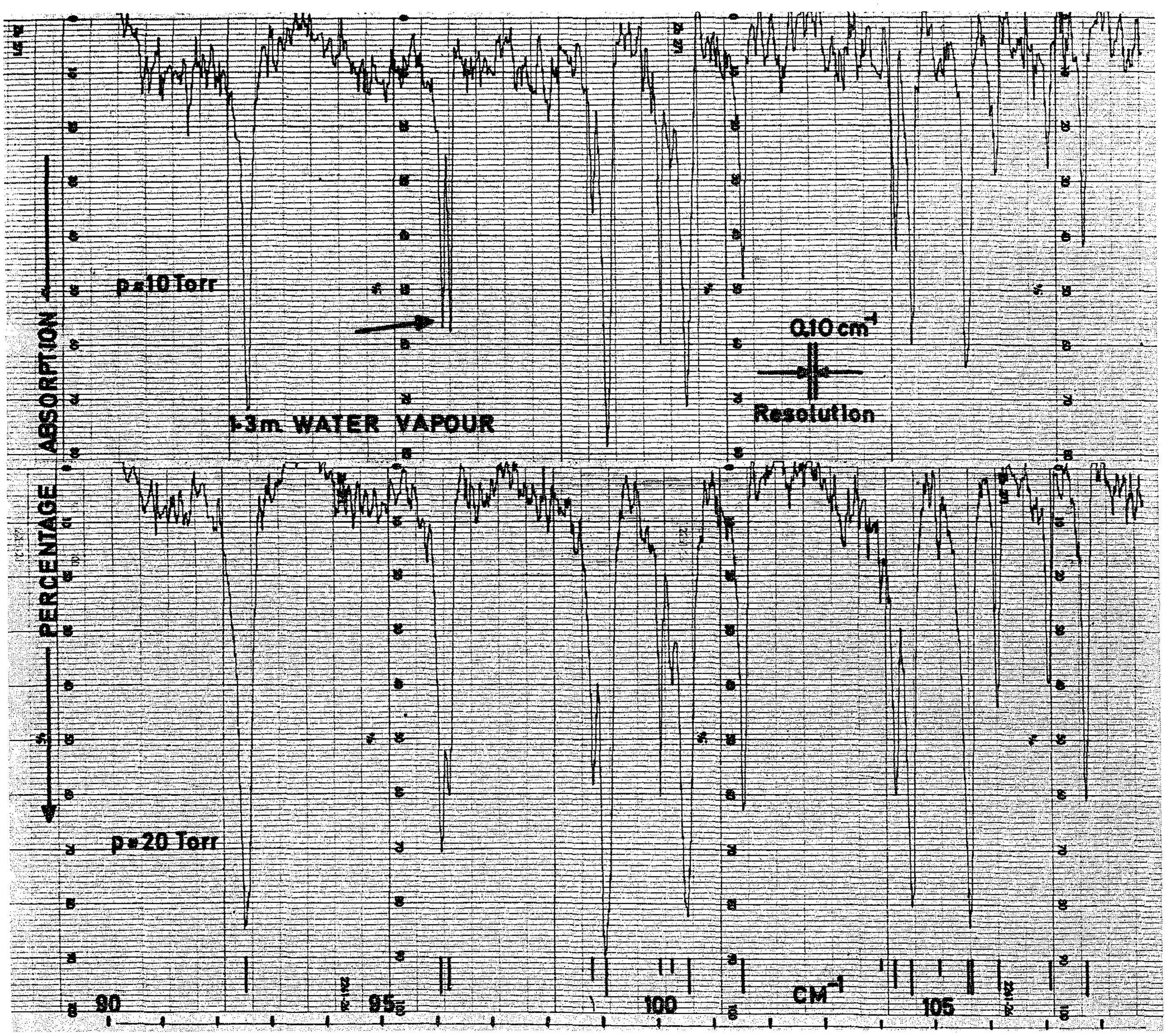


Fig. 8. Details from two high resolution water vapor spectra recorded at different vapor pressures, using the FIR 30 interferometer. Each double-beam spectrum was recorded to 0.10 cm^{-1} resolution (10 cm optical path difference) in 90 minutes total scanning and plotting time. The splitting of the (arrowed) doublet at 96 cm^{-1} is 0.15 cm^{-1}. The theoretically predicted frequencies and relative absorption strengths of these H_2O pure rotational transitions are indicated by the strokes on the lower trace. (R.T. Hall and J.M. Dowling, J. Chem. Phys. 52, 1161, 1970)

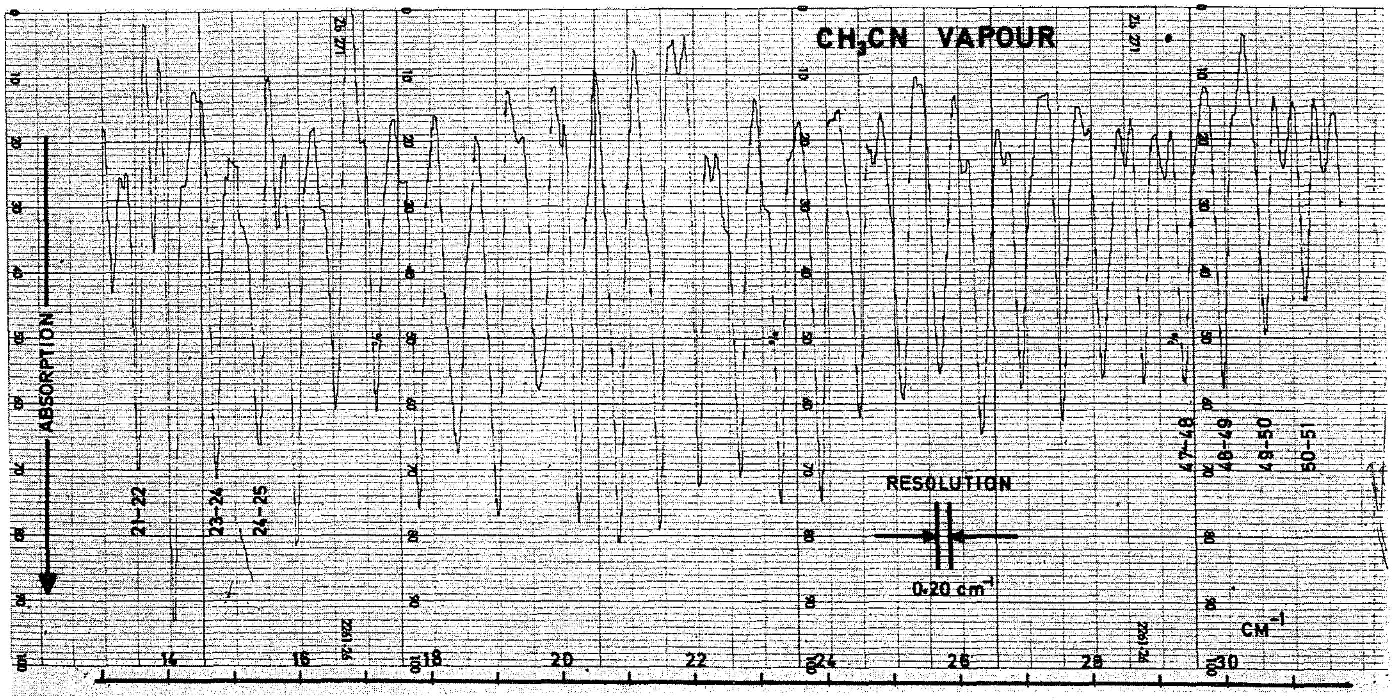


Fig. 9. Portion of very low wavenumber pure rotational spectrum of acetonitrile vapor recorded at 0.20 cm^{-1} resolution in ~ 40 minutes total scanning and plotting time. The pure rotational absorption lines of regular spacing ~ 0.6 cm^{-1} are clearly resolved.

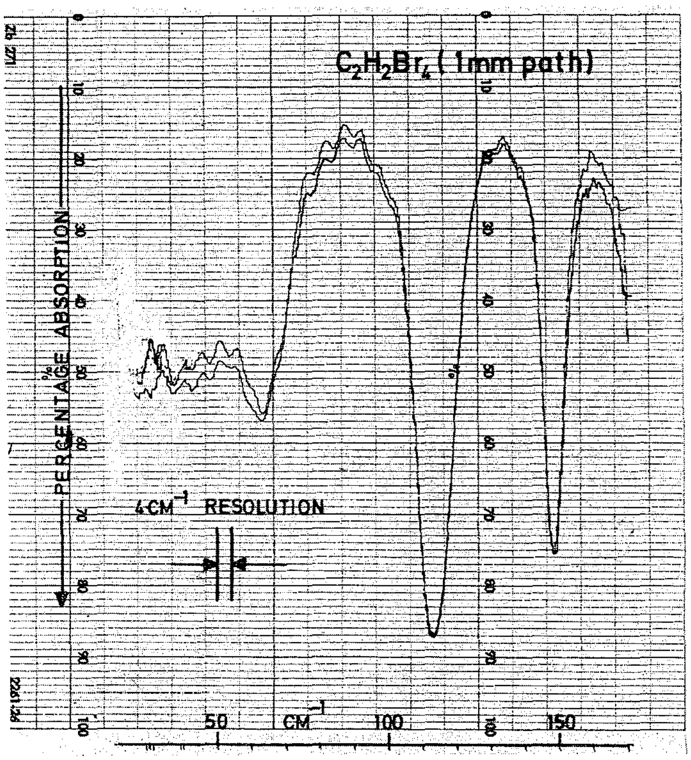


Fig. 10. Transmission spectra of liquid sym-tetrabromoethane recorded in a 1-mm-thick liquid cell. Each double-beam spectrum was obtained in ~ 10 minutes scanning and plotting time.

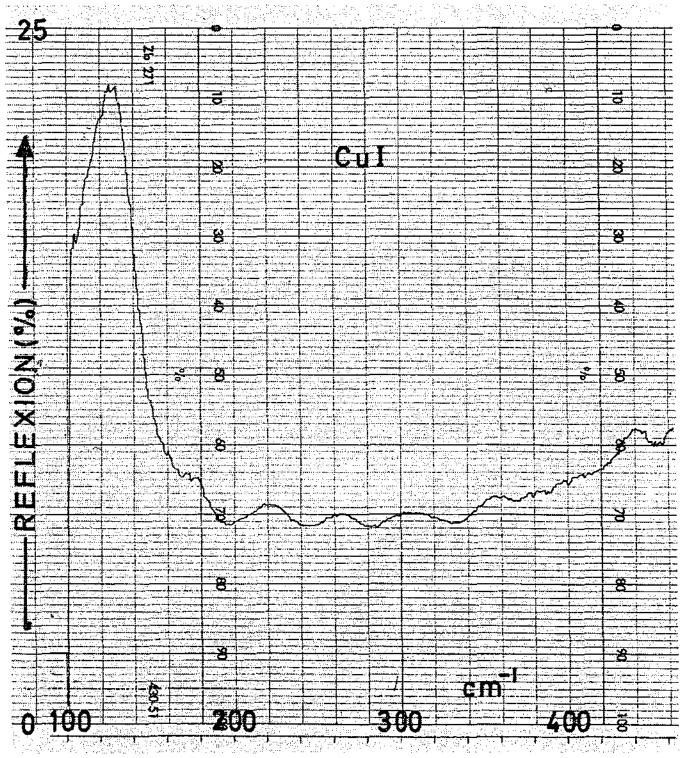


Fig. 11. Reststrahl reflection spectrum of a 3 mm diameter copper iodide disc recorded at 10 cm^{-1} resolution, in a total time of 6 minutes. (Sample by courtesy of Dr. H.P. Geserich, University of Karlsruhe).

Fig. 10 shows two consecutively recorded liquid transmission spectra which indicate the typical intensity reproducibility of ~1-2% at moderate resolution in regions where the beam splitter has optimum transmission. Reproducibility deteriorates at both extremities of the spectrum, where the signal/noise is low in the reference beam.

An advantage offered by the compact image optics of the FIR 30 is that very small samples may be studied without excessive loss in energy. Fig. 11 shows a typical example of a reflection spectrum recorded from a 3 mm crystal. Under optimum conditions acceptable spectra can be recorded for samples as small as 1 mm.

Another important feature of the FIR 30 interferometer is its adaptability to many standard spectroscopic accessories. Solids and liquids may be studied over a wide range of temperatures.

Fig. 12 demonstrates the instrument for polarized transmission or reflection studies, in this case for a polymer sample. For Fig. 13 the FIR 30 is taken to its upper limit of 1000 cm^{-1}. One paradox of slow-scanning Michelson interferometers of this type is that although very much better signal/noise is available at higher wavenumbers, interferogram scan speeds must be slowed down at high frequencies; the high periodicity of oscillation of the interferogram function about its central maximum necessitates a low scan speed – time constant combination if the central peak is to be recorded without distortion. Consequently, high resolution spectra can be recorded much faster in the more difficult low wavenumber region than in the high wavenumber region.

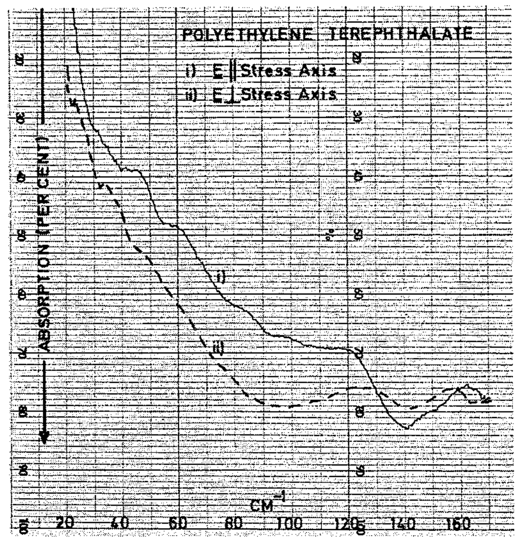


Fig. 12. Polarized transmission studies of a pre-stressed polyethylene terephthalate foil recorded at 10 cm^{-1} resolution in scanning times of 6 minutes each. The difference between the E∥ and E⊥ spectra is associated with the selective excitations of crystalline and amorphous type lattice structures. (Sample by courtesy of Dr. W. Frank, University of Ulm).

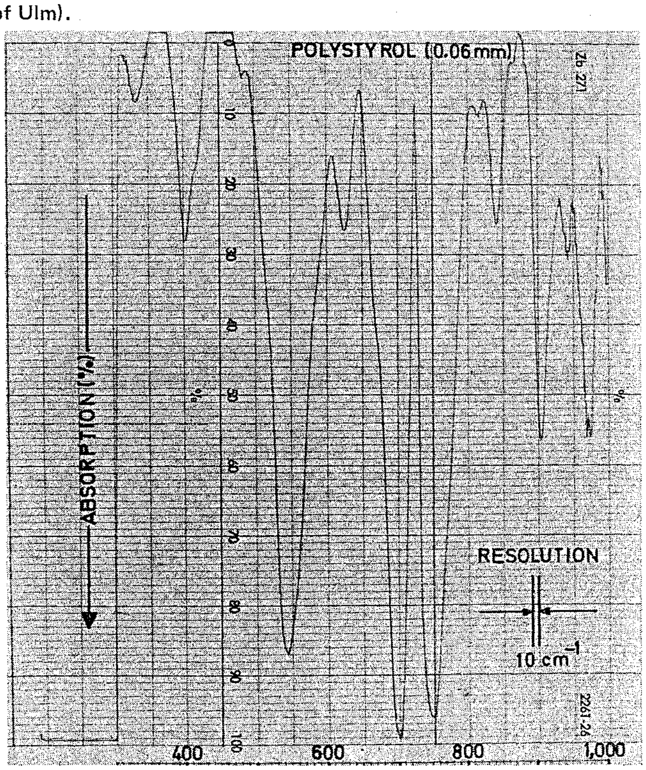


Fig. 13. Transmission spectrum of a 0.06 mm thick Polystyrol film recorded at 10 cm^{-1} resolution in a total scanning time of ~ 12 minutes.

We have attempted to outline in a general fashion some of the problems encountered with heretofore commercially available far-infrared Fourier spectrometer systems, and to establish the way in which the Polytec FIR 30 spectrometer has been designed to overcome such difficulties. From the point of view optics-mechanics, the unique FIR 30 automatic beam splitter changer mechanism has not only led to a great saving of operating time but has obviated the need to open up any part of the instrument except the sample chamber. This not only leads to better instrumental reproducibility but makes the Fourier spectrometer valuable to a larger number of laboratories. In a similar fashion, the versatile two-beam sample chamber provides great flexibility for the most diverse studies, with optimum convenience.

The IR 50 Golay detector has proved to be outstanding and reliable with the FIR 30 and other far-infrared interferometers of this type, and appears to be the best room temperature detector currently available.

The real-time method of Fourier transform computation has brought coupled bonuses of instantaneous spectrum display and all its inherent advantages, together with the potential of attaining a large number of spectrum points from a relatively inexpensive small memory computer. One restriction of the real-time system to date is that it has not been programmed (and would need larger memory capability) for complex Fourier transformation computations of refractive index. However, the raw interferogram data tapes are always available to be so processed on a large general purpose digital computer, as and if required.

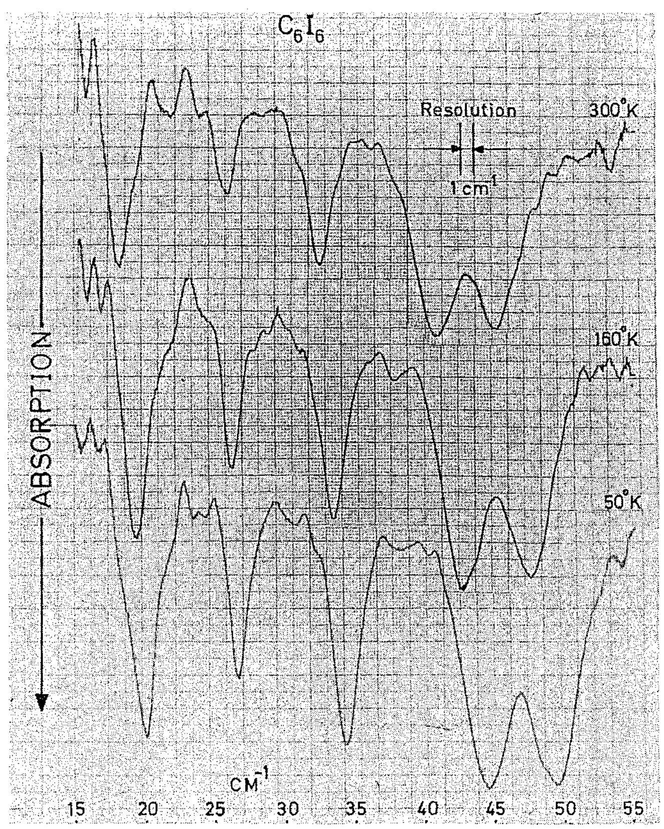


Fig. 14. Low wavenumber external vibrational spectra of solid hexiodobenzene recorded at 1 cm^{-1} resolution in approximately 15 minutes total scanning and plotting time each, using the FIR 30 interferometer and CRYODYNE 20 Cryocooler unit. (Sample by courtesy of Dr. M. Dakkouri, University of Karlsruhe).

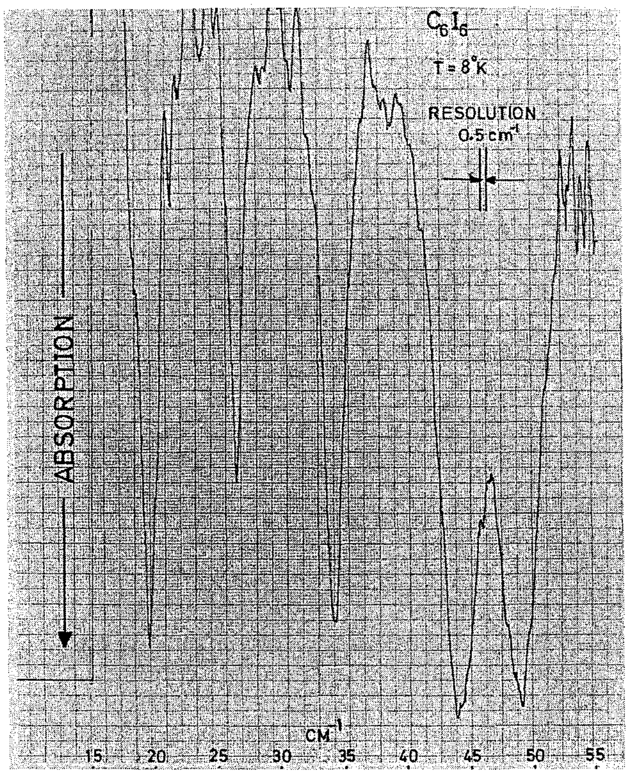


Fig. 15. Very low temperature C_6I_6 transmission spectrum recorded at 0.5cm^{-1} resolution in ~30 minutes scanning and plotting time.

VARIATION OF C_6I_6 EXTERNAL VIBRATIONAL FREQUENCIES WITH TEMPERATURE.

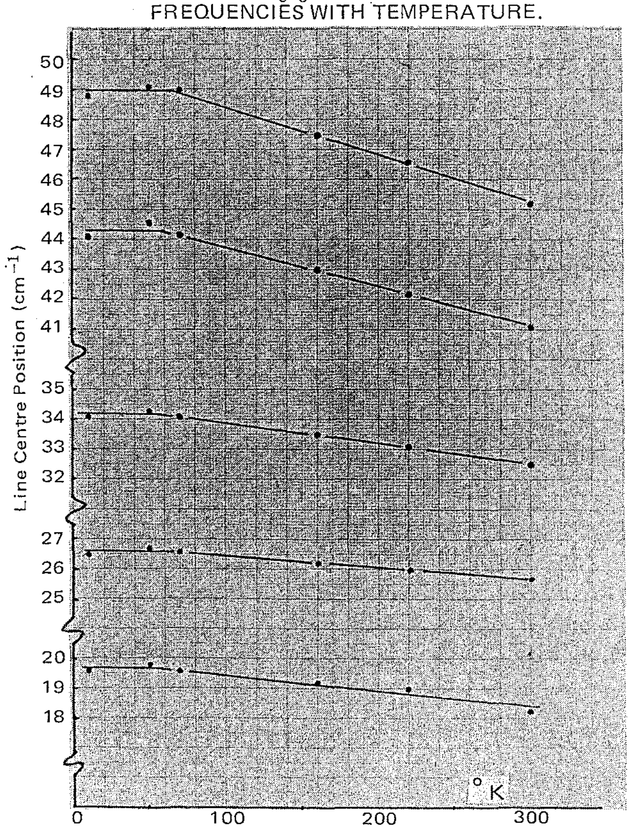


Fig. 16. Measured variation of C_6I_6 low wavenumber external vibrational frequencies with temperature.

As evidenced by the wide range of topics currently under investigation in the far-IR, some of which are listed on page 12,there will be an increasing demand for instrumentation covering this spectral region. Until physicists finally realize their long-talked-of dream to conceive a continuously tunable narrow-band light source (or detector) for the whole near and far-IR spectral regions, Fourier spectrometers must fill this need for some years to come.

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While there has been a tremendous proliferation of publications concerning all aspects of far-IR spectroscopy and Fourier spectroscopy in the last decade, the following references might serve as useful background material for the reader interested in making closer acquaintance with some of the topics discussed here.

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