

THE MEASUREMENT OF INFRARED SPECTRA WITH DIGITALLY RECORDING SPECTROPHOTOMETERS*

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INTRODUCTION

Before proceeding to our main topic, I want first to discuss the impact of the electronic computer on molecular spectroscopy. This is not intended to suggest that the use of a computer is an innovation in spectroscopic research. Many in this audience have employed electronic computers for several years to aid in the evaluation of molecular force fields, to calculate normal coordinates of the vibrations of polyatomic molecules, and to compute molecular energy levels by quantum mechanical methods. Until recently, however, the necessary computing facilities could be found only in a few specially equipped laboratories. In the two years that have passed since the Copenhagen Congress we have witnessed an explosive expansion in the availability of large electronic computers so that it is fast becoming the accepted practice to have extensive computation facilities as part of the standard services of the spectroscopy laboratory.

Molecular spectroscopists use electronic computers in three distinct ways:

- (i) For data acquisition
 - (ii) For data storage and retrieval
 - (iii) For data analysis and interpretation
- and it is convenient to consider these separately.

Data acquisition

Here the computer is an integral part of the apparatus for measuring the spectrum, and, subsequently or simultaneously, it operates on the raw data by appropriate techniques of numerical analysis. The quality of the data can be improved by applying corrections for wavenumber and intensity calibration errors, for distortion caused by the finite spectral slit width, by random noise, by errors in the evaluated sample path length, and by other uncertainties in the experimentally-measured parameters. We shall look into these problems in detail later.

In a more sophisticated manner there could be real time feed-back from the computer to control the spectrophotometer during the measurement of the spectrum. This might permit adjustment of such instrumental variables as scanning rates, encoding intervals, mechanical slit widths, and the electronic filtering circuitry to optimize the quality of the raw experimental data. To my knowledge this stage of computer-spectrometer coupling has

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not yet been achieved in infrared spectrophotometry, though it has in X-ray crystallography, where, in several laboratories, X-ray diffraction cameras are computer controlled so that the crystal orientation is optimized for the diffraction from each crystal plane.

We can also include in category (i) the Fourier transformations of interferometric infrared spectroscopy, and the evaluation of infrared band shapes and intensities from dispersion measurements and from attenuated total reflectance measurements, using the Kramers–Kronig equation.

Data storage and retrieval

In handling data storage and retrieval, the computer operates on the corrected spectral data to cast it into an optimal format for efficient storage in a library file. From this file it can be called back into the computer, in whole or part, for further numerical analysis; for matching with other spectra by pattern recognition techniques, by group frequency classification for structure identification, or for quantitative analysis.

Data analysis and interpretation

In this third category we are concerned with the more fundamental computations of theoretical molecular spectroscopy. Here the computer is used as an aid in the interpretation of the molecular structure and of the vibrational and rotational behaviour of the molecule by feeding in parameters derived from the experimentally-measured spectrum.

In his preceding talk, Professor Mills¹ has illustrated how such computer-aided techniques are providing a deeper understanding of the rotation–vibration structure in the spectra of simple molecules. Later at this Congress Dr. Califano² will discuss the use of computer-aided techniques to evaluate the force fields of more complex molecules. In another theoretical field, typified by the work of Bratoz³, Gordon⁴, and Shimizu⁵, computer-aided techniques are being applied to the theory of infrared band shapes in liquid-phase systems. Developments in this field will be discussed later at this Congress by Professor Crawford⁶. You will see therefore that category (iii) is well illustrated in the contributions of other speakers at this Congress, and I propose to restrict the remainder of my talk to categories (i) and (ii). We shall also limit ourselves to condensed-phase systems, principally solutions.

A further reason for this selectivity is that the logistical relationships between the spectroscopy laboratory and the computation centre differ as between categories (i) and (ii), on the one hand, and category (iii) on the other. This is because (i) and (ii) involve the interaction of the spectrophotometer with the computer, whereas the actual infrared instrumentation plays no direct part in (iii). The linkage of the spectrophotometer with the computer, either physically or through appropriate programme routines, creates several problems that have still not been satisfactorily solved.

Computer–spectrometer interactions

These problems are not specific to infrared spectrophotometry, and they arise wherever attempts are made to link a computer to an electrical or mechanical analogue recording system from which the output is subsequently digitized at constant time intervals in the fractional second to minute range.

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Mass spectrometers, ultraviolet spectrometers, Raman spectrometers, X-ray diffraction cameras and gas-phase chromatographic recording systems all come within this classification. Recognizing a common interest in these problems, a loosely knit organization calling itself "The Study Group for Computer Aided Experimental Spectroscopy" came into being in North America in the spring of 1966. Meetings have been held at the National Research Council of Canada, Ottawa (July, 1966) and at the General Electric Research and Development Center, Schenectady, New York (July, 1967). Each meeting was attended by about thirty investigators who were actively engaged in spectrometer-computer interfacing problems in the various fields listed above, and several computer technologists and numerical analysts also participated. I think it will be of interest for me to summarize the consensus of this group concerning the problems of cooperation between the spectroscopy laboratory and the computation center. I am helped in this by the three cartoons illustrated in *Figures 1-3* which were kindly lent to me by Dr. Savitsky.

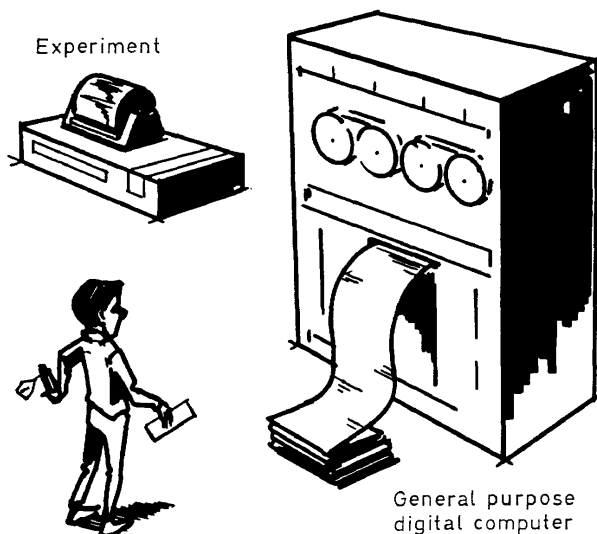


Figure 1

Figure 1 summarizes what is, in many respects, the ideal relationship between the spectroscopist and the computer. He has his own private computer sitting right beside his spectrometer. Expressed more realistically, he has direct personal access to a computer in close physical proximity to the spectroscopy laboratory. We operated under these conditions over the period 1963-1965, and it proved a very happy and fruitful arrangement during the initial stages of developing programmes for correcting slit function distortions^{7, 8}. The difficulty is that only a small computer can be made available in this way. We were fortunate in obtaining the part-time use of a Scientific Data System Model 920 computer. This permitted us to develop basic programmes on simple simulated spectra, but it lacked both

the speed and the memory capacity to apply these programmes to real spectra. Nevertheless, *Figure 1* illustrates a very attractive situation, and one which we often recall nostalgically.

In *Figure 2* we see what happens when the large computer enters the scene. The spectroscopist finds himself separated from the computer by a wall of technical complexities and administrative red tape, and he must communicate with the computer through a chain of intermediaries. This illustrates the situation in which many spectroscopy laboratories find themselves to-day. Much useful work can be accomplished under these

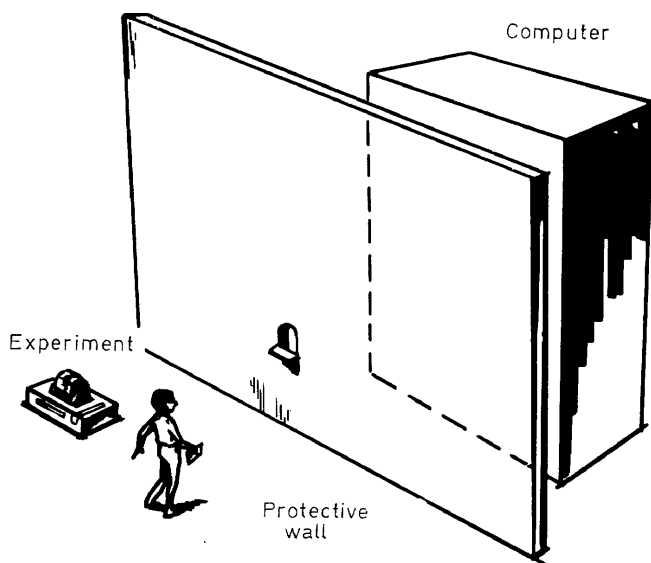


Figure 2

conditions provided there is good liaison and technical understanding on both sides of the partition. Most of the computations of theoretical molecular spectroscopy are currently made in this manner. The consensus of our Study Group is that this situation can only be regarded as satisfactory where the computer programmes are stabilized and not subject to continuous developmental modification. Force field calculations may provide an acceptable example. In our laboratory Professor Krueger* and Dr. Fuhrer have spent the past year evaluating force fields for two diethyl ether conformers, and three cyclohexanone conformers using the programme developed by Schachtschneider and Snyder⁹. Here the fully tested and operative programme was stored in the disc memory of the computer, and the spectroscopic experimentation principally involved small numerical adjustments to the input parameters, associated with modifications in band assignments, input force constants, and the molecular geometry.

* On sabbatical leave from the University of Calgary.

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The coupling of the spectrometer to the computer, either physically or by appropriate programming, is more difficult to achieve under these conditions. We are doing this, and the spectra I shall discuss later were all obtained in this manner using an I.B.M. 360/50 computer, but at times it was a harassing experience, and it has worked only because we have eventually achieved a good liaison with the computation centre. Systems analysts and technicians assigned to our project by the centre have spent sufficient time in our laboratory to acquire some knowledge of the measurement of infrared spectra, and a general feeling for what is happening on our side of the partition. My two spectroscopy technicians, for their part, are familiar with the operating procedures at the computation centre, and they understand enough about the internal logic of the programmes to collaborate intelligently with their opposite numbers at the centre.

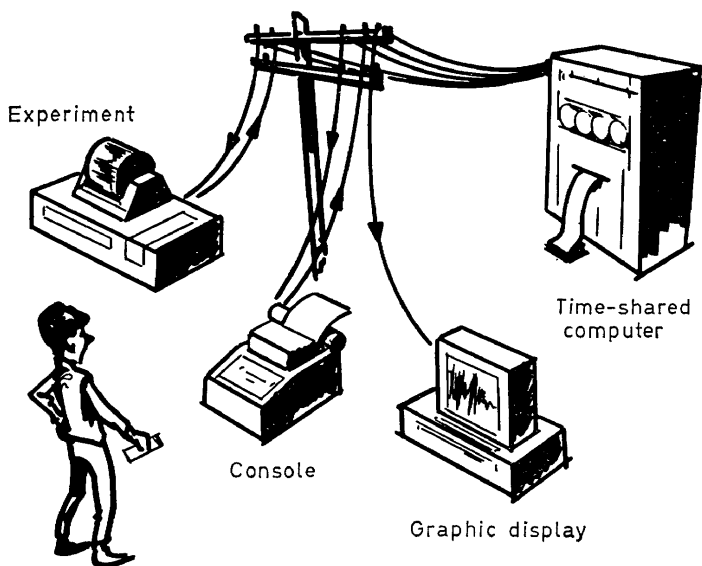


Figure 3

We feel emphatically that no computer programme can be used safely and effectively unless the spectroscopist has sufficient command of the programme language to understand at least the gross features of the internal structure of the programme. He must also have the facility to make minor programme modifications himself. Life can become extremely frustrating if the spectroscopist needs resort to a professional programmer whenever changes in the programme are called for.

A good deal is now being heard about time-shared computation systems, and this situation is illustrated in *Figure 3*. This provides for direct access from the spectroscopy laboratory into a large remote computer, and feed back of the computer output directly to the spectroscopist. The basic feature of this system, which makes it an economic possibility, is the provision for

several such laboratory terminals to be linked simultaneously to one computer. Here we must qualify the use of the word simultaneously. The essence of the method is that the computations received from the numerous laboratory terminals are dealt with consecutively in quick succession. They are stored in memory banks and each is cycled into the actual computation unit of the computer according to a pre-arranged scheduling system. Twenty or more terminals can be linked into one computer. A typical system, operating in an industrial analytical laboratory can handle the output from a dozen gas chromatographic recorders, an n.m.r. spectrometer, two X-ray diffraction cameras, an ultraviolet spectrophotometer and four infrared spectrophotometers.

On first impression such a system appears to restore the original happy situation in which the spectroscopist regains personal control of his own computer, and a large one to boot. For the present however there are difficulties in operating such a time-shared system in a manner compatible with the demands of a spectroscopic research laboratory. It may work satisfactorily under the conditions existing in an industrial analytical laboratory, where the recording instrumentation is used in a routine fashion and the demands on the computer from each terminal are stabilized and relatively constant. In a research institution there are likely to be continuous and widely-fluctuating changes in the demands on the computer facilities from the various terminals, and this creates conflicts in the programming priorities.

The solution could be the introduction of the 'intelligent' terminal. This requires putting back into the spectroscopy laboratory a small computer linked to the larger one at the computation centre. The small computer will accept the data from the spectrometer, edit it, convert it to a standardized format, and, if necessary, store it until the main computer is ready to accept it. Such a system to a large extent frees the spectrometer from the rigid time demands of the large computer, and permits versatility in handling the spectrometer output without making constantly-changing demands on the main system.

A SYSTEM OF AUTOMATED INFRARED SPECTROPHOTOMETRY

I want to pass on now to describe a system of automated infrared spectrophotometry that we have assembled at Ottawa during the past two years. This has been developed as a prototype of a programme-linked spectrometer-computer system which is of general application and can be easily replicated. As far as possible we have used commercially-available spectroscopic and computing equipment; the only unit we have found it necessary to construct ourselves is a high-speed rotating-sector photometer which will be discussed later. We have kept in mind the need to obtain a conventional chart record of the spectrum simultaneously with the encoding of the tape record, and to maintain a recording speed compatible with current practice in the chemistry laboratory. We have standardized on a recording speed of $40 \text{ cm}^{-1}/\text{minute}$ and an encoding interval of 0.5 cm^{-1} throughout the spectrum. A complete spectrum covering the range $4000\text{--}280 \text{ cm}^{-1}$ can be recorded in about three and a half hours, including the ancillary control

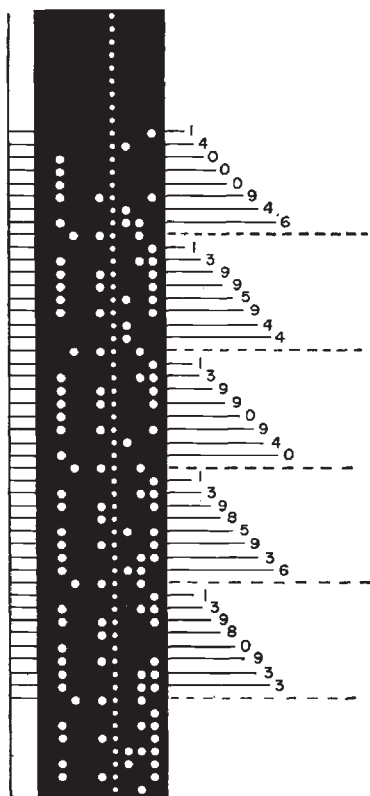


Figure 4. Encoded paper tape; 14000946 signifies a transmittance of 0.946 at 1400.0 cm^{-1} and is followed by the end-of-word character

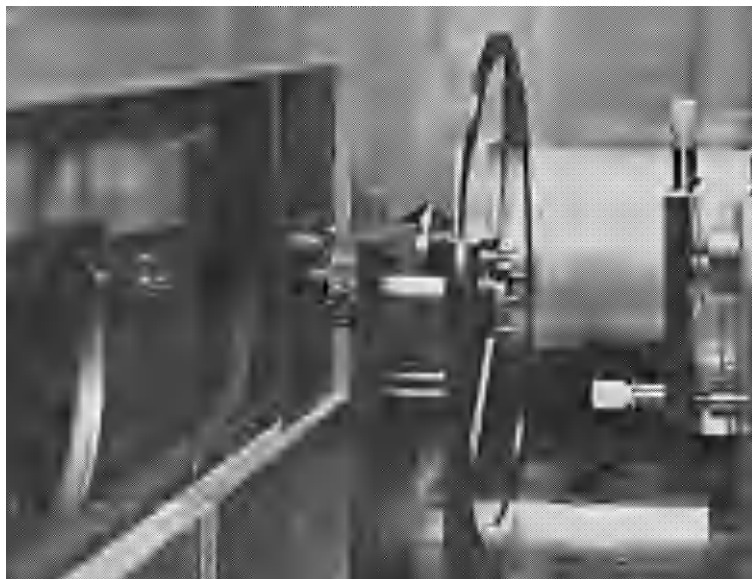


Figure 6. The cell compartment of the spectrophotometer with the control rotating-sector photometer in the sample beam



Figure 9. The cell compartment with small calibrating sector photometer located at the position of the sample cell

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measurements. A standard Perkin-Elmer Model 521 spectrophotometer is used, linked to a Perkin-Elmer Digital Data Recorder and Teletype 8-hole tape punch (Model BRP-E11). In addition to the drum recorder, integral to the spectrophotometer, a second chart can be recorded simultaneously on a slave recorder. This second record carries fiduciary marks along each edge, which are triggered by the signal actuating the tape punch. In this way an expanded visual recording of the spectrum is obtained which can be compared directly with the punched tape.

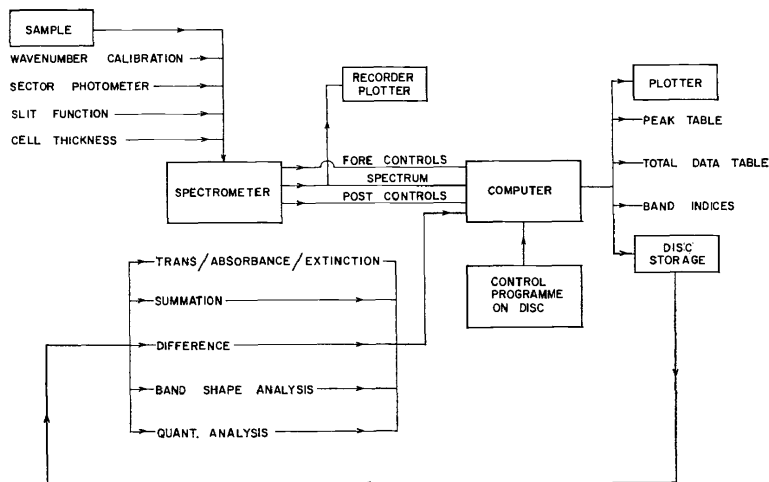


Figure 5. Block diagram of the spectrophotometer-computer system

A representative section of the tape record is shown in *Figure 4*. It consists of eight-digit blocks composed of a five digit wavenumber and a three digit transmittance datum, with each block separated by an end-of-word signal. A diagram of the complete analysis system is shown in *Figure 5*. Much of this diagram is self-explanatory and we need only deal with a few of the less obvious features. This system is now operating routinely, and the computer programme, written in Fortran IV, is available^{10,11}. The programme has been broken up for publication purposes into about twenty-two separate and independent modular units which can be linked by common card input and card output formats in a building block manner; alternatively they may be introduced as a set of subroutines into a more complex programme.

Intensity calibration with rotating-sector photometers

The calibration of the intensity scale involves the use of the high-speed rotating-sector photometer illustrated in *Figure 6*. The sector wheel is located in the sample beam between the source housing and the space occupied by the cell. Two interchangeable wheels are used, one having approximately 80% transmission, and the other approximately 20%. The sector transmissions were calibrated by two independent methods which agreed within

$\pm 0.02\%$ T for *white visible radiation*. Details of the structure of these sector photometers, and of the calibration methods have been described¹². The manner in which the sectors are used is illustrated in *Figures 7* and *8*, with reference to a section of the spectrum of a carbon disulphide solution of

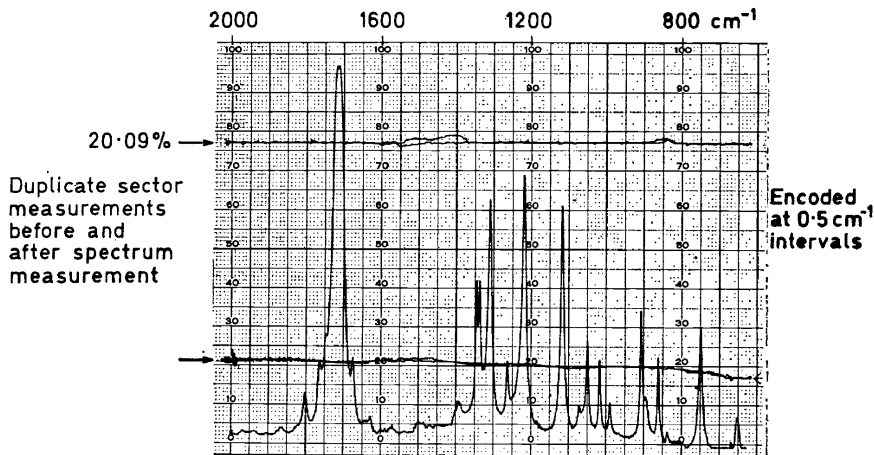


Figure 7. Spectrum of cyclohexanone in carbon disulphide solution as directly recorded on the spectrophotometer simultaneously with its tape encoding

cyclohexanone; the same spectrum will also be used for other illustrative purposes later. Initially, with solvent in both cells, sector measurements are made across the spectrum at 20% and 80% transmission, encoding at 10 cm^{-1} intervals and at ten times the standardized recording speed. The solvent in the sample cell is then replaced by the solution and the spectrum measured under the standardized encoding conditions. Finally the solvent is again introduced, and the two sets of sector measurements repeated, so that in all five tape records are obtained.

These paper tapes are next converted off-line to a magnetic tape from which the computer interpolates the spectral transmission against the mean of the 'fore' and 'post' sector control runs; this yields the computer-plotted 'normalized' spectrum shown in *Figure 8*. The programme provides for tolerance checks on the sector intensity measurements, and it rejects accidental 'catastrophic' error punches such as may result from line surges or other extraneous interference. In the normalization procedure, it is not assumed that the intensity interpolation need be linear. The photometric system is calibrated with a set of eight smaller sectors which can be located at the position of the sample cell (*Figure 9*)*. A small parabolic correction is needed and is entered into the programme by a punched card. This calibration curve is shown in *Figure 10*, and a residual error curve is shown in *Figure 11*. The significance of the parabolic error has been discussed¹² but is not yet understood. It may indicate deficiencies in the optical behaviour of the sectors, associated with their rotation, infrared reflectivity or mode of

* These small sectors were obtained from Research and Industrial Instruments Co., London, England, and are now marketed by Beckman Instruments, Inc.

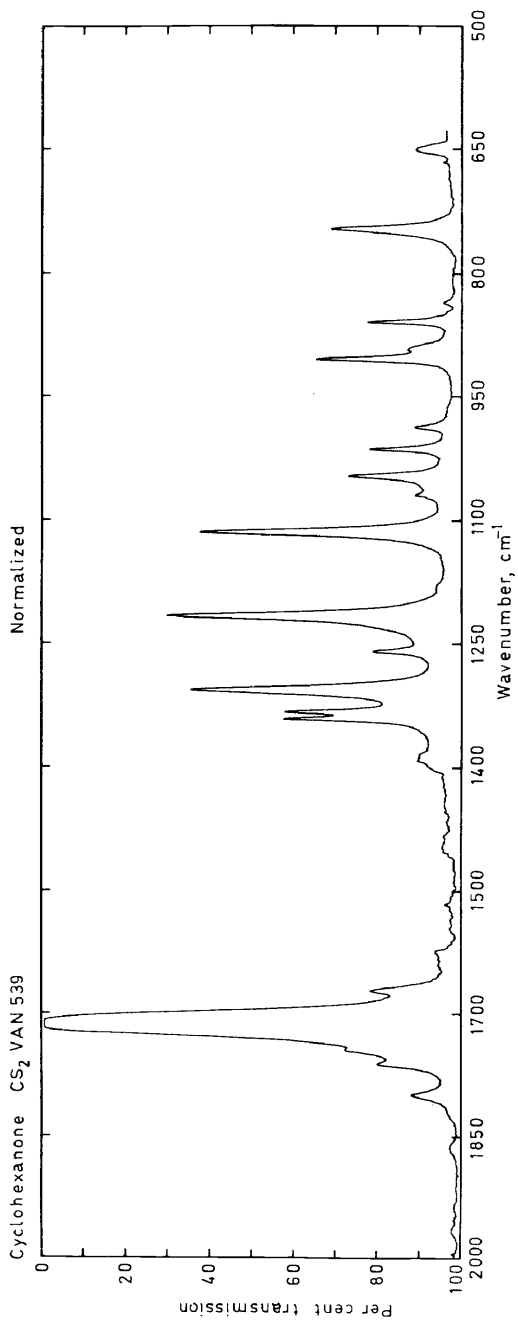


Figure 8. Computer-plotted 'normalized' spectrum from the data of Figure 7 with ordinate scale in percentage transmission

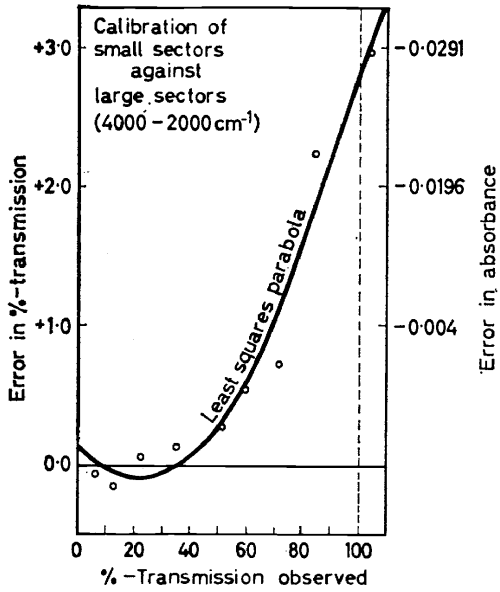


Figure 10. The spectrophotometer intensity calibration curve

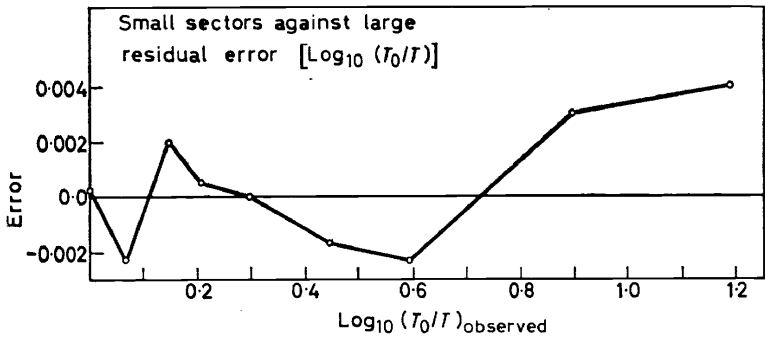


Figure 11. The residual intensity error curve for the small sectors after application of the parabolic correction

interaction with the radiation beam, and it is clearly necessary to determine the cause before applying the method more generally. Repeated calibration tests¹², made over a period of one year, suggest a reproducibility of about $\pm 0.4\%T$ in the absolute accuracy of the photometric measurements.

In addition to the normalized, plotted spectrum, the computer prints a table of the positions and intensities of the peaks, interpolated by a cubic function to $\pm 0.1 \text{ cm}^{-1}$ and also a complete tabulation of all the normalized data points. If desired, these data points can also be recorded permanently

on magnetic disc in the memory storage of the computer from which they can be recalled, over any requested wavenumber range, for further analysis, or for comparison with other spectra.

Wavenumber calibration

The wavenumber calibration correction is currently obtained by feeding the computer cards listing the measured positions of seven bands in the spectrum of liquid indene^{13, 14}. From these the computer generates a set of linear correction functions. These are applied to the listing of the peak positions, and, in addition, a separate table of the wavenumber corrections at 100 cm^{-1} intervals is printed with each normalized spectrum. Using this method of wavenumber correction, the standard deviation in the corrected peak positions is 0.52 cm^{-1} over the range 4000–2000 cm^{-1} where the spectrometer operates in the second order of the grating, and 0.34 cm^{-1} between 2000 and 650 cm^{-1} . The present lack of acceptable wavenumber standards below 650 cm^{-1} limits the value of corrections in the 650–280 cm^{-1} range, though provision for this region is included in the programme.

This method of wavenumber calibration is a provisional expediency and we are developing a more effective one, based on the use of a set of interference fringes obtained with a germanium interferometer cell. These fringe patterns are shown in *Figure 12*. They hold their positions well, and we are currently developing a method whereby the fringe pattern can be locked into register with a pair of water vapour bands to provide a series of fixed calibration points at about 20 cm^{-1} intervals across the spectrum. R. O. Crisler, using similar fringe patterns has obtained a calibration accuracy of about 0.25 cm^{-1} on sharp peaks in condensed phase spectra¹⁵.

Finite spectral-slit correction

The final step is the application of a correction for the finite spectral-slit distortion. Details of the method have been published^{7, 8}, and, under the conditions used, it is estimated that about 90% of the slit distortion is eliminated. Our present operating system requires a repass of the normalized data through the computer for this purpose; the final 'slit deconvoluted' spectrum so obtained is shown in *Figure 13*. A triangular slit function is assumed, and the spectral slit half-band width is calculated from the geometrical optics of the spectrophotometer¹⁶. The spectrum shown in *Figures 7, 8 and 13* was measured at a spectral slit width of 1.5 cm^{-1} and the effect of the slit correction is about 2%T on the narrower bands; it is not prominent in the plotted curve but it is evident throughout the spectrum in the tabulated data, or when plotted on an expanded ordinate scale*. There would be no technical difficulty in incorporating this step into the preceding stage of computation, so as to combine it with the wavenumber and intensity calibration and ordinate scale normalization. However, though the slit deconvolution analysis does eliminate much of the spectral slit distortion, it may be introducing secondary distortion of a kind not yet fully understood,

* Examples of spectra measured at 3 cm^{-1} spectral slit width, and at 1.5 cm^{-1} spectral slit width on an expanded chart scale, have been reported in references 7 and 12 respectively.

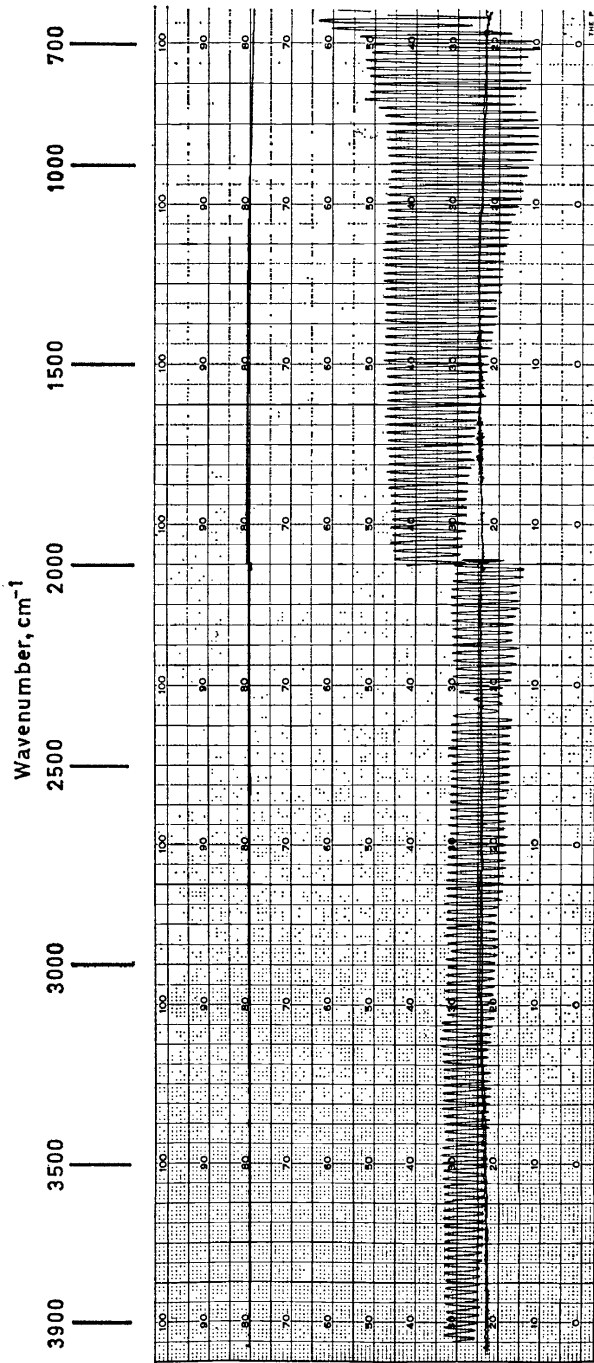


Figure 12. Interference fringes from germanium interferometer cell

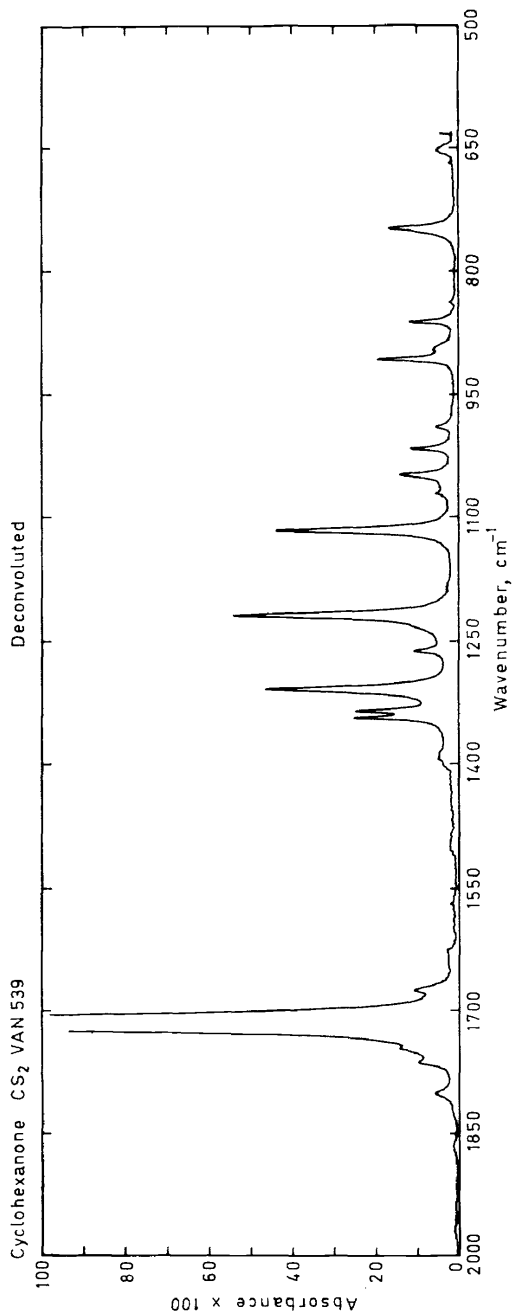


Figure 13. Computer-plotted 'slit deconvoluted' spectrum from the data of Figure 7 with ordinate scale in absorbance $\times 100$

and it therefore seems prudent to distinguish spectra that have been subject to slit deconvolution from the 'normalized spectra' that have been adjusted only for ordinate and abscissal calibration errors and non-linearity.

THE STORAGE AND RETRIEVAL OF HIGH DENSITY SPECTRAL DATA

Before concluding, let us consider some of the implications of computer encoding techniques on the storage and retrieval of infrared spectral data. As the quality of the data improve, efficient storage becomes an increasingly demanding problem. At one time it sufficed to tabulate only the band peak positions, and this information together with a simple chart, which did not necessarily carry an ordinate scale, was adequate to convey all the experimentally significant information about the spectrum. Many infrared spectra listed in present day compendia attempt no more than this.

As the resolution improves, and the instrumental errors are brought increasingly under control, it becomes important that storage files of infrared spectra retain information about the band shapes. Our experience with encoding indicates that to register all the significant information about the band contours that we can observe visually in chart records of condensed phase spectra, the coarsest permissible encoding interval is 0.5 cm^{-1} throughout the spectrum. A minimum of 380 cards is needed to store such a spectrum on punched cards over the range $4000\text{--}200 \text{ cm}^{-1}$. A card coded in this manner is virtually unreadable without a mechanical listing device, as this constitutes a maximum density storage format and the card is covered with a solid block of transmittance data. It makes no provision for wavenumber calibration adjustments as it must be assumed that the encoding wavenumber intervals are constant. To tabulate both wavenumber and transmittance data on a card in a format easily readable on inspection, 950 cards per spectrum are required. If this data is to be plotted on a chart at a line density of 2 points/mm a chart 3.8 metres long is required. This chart length can, of course, be reduced for storage purposes by micro-film techniques, but it must still be enlarged back again to the original size for reading, if the full information content is to be retained.

An alternative approach to the storage of spectral data would be to describe the spectrum by an overlapping set of symmetric mathematical bands. Ideally these should have physical significance, and be identified with the solvent-broadened bands corresponding to pure or mixed normal vibrations. This however is not a strict requirement for storage purposes; the component band parameters, which we shall call 'spectral indices' can be regarded as purely empirical quantities. Stone¹⁷ and Papoušek and Plíva¹⁸ were among the first to use computer-aided methods of non-linear least-squares approximations to fit infrared band envelopes in this manner, and in our laboratory Dr. Pitha has recently developed three efficient computer programmes for this purpose^{11, 19, 20}. Bell and Biggers have developed a similar programme for electronic spectra²¹.

The Cauchy and Gauss functions most readily suggest themselves for this purpose (*Figure 14*). Both of these require three adjustable parameters to define them specifically, so that a band system characterized by N peaks or

Cauchy (Lorentz)

$$f(v)_c = \frac{X_1}{[1 + X_3^2(v - X_2)^2]}$$

Gauss $f(v)_G = X_1[\exp\{-X_4^2(v - X_2)^2\}]$

Product $f(v)_p = \frac{X_1}{[1 + X_3^2(v - X_2)^2]} \cdot \exp\{-X_4^2(v - X_2)^2\}$

Sum $f(v)_s = \frac{X_1}{[1 + X_3^2(v - X_2)^2]} + X_5[\exp\{-X_4^2(v - X_2)^2\}]$

Figure 14. Band shape functions

inflections would need $3N$ 'spectral indices' for a full description. In our experience a satisfactory fit cannot generally be obtained with these simple functions and the Cauchy-Gauss product function with four variables is much more satisfactory (Figure 14). The computer-plotted spectral chart of cyclohexanone over the range $1400-630 \text{ cm}^{-1}$, as obtained from 1540 data points encoded at 0.5 cm^{-1} intervals, is shown in Figure 15, and may be compared with the calculated curve shown in Figure 16 which was obtained with 77 'band indices' using Pitha's programme. This curve is based on a breakdown of the band envelope into 19 component Cauchy-Gauss product functions, with one additional degree of freedom to permit a parallel displacement with respect to the base-line. The difference curve, on a fivefold expanded ordinate scale, is shown in Figure 17. More recent work²⁰ suggests that the Cauchy-Gauss sum function (Figure 14) may be more effective than the product function. The sum function provides for a fifth variable, but on single-band envelopes generated by convoluting a Cauchy curve with a triangular simulated slit function, the sum function fits better than the product function even if the number of variables is reduced to four by freezing the x_3/x_4 ratio²⁰.

The degree of data condensation that can be achieved by storing spectra as indices instead of encoded data points is illustrated diagrammatically in Figure 18. Obviously such a technique must be refined considerably before it can be recommended as an acceptable alternative to the storage of the 'real' spectral data; furthermore it is not likely to be acceptable on economic grounds until the cost of computation is further reduced. The storage of spectral indices does have the advantage that it readily permits the spectrum to be regenerated in any selected ordinate and abscissal unit, and on any scale desired. This could eliminate several thorny problems that currently complicate the establishment of a uniform and generally acceptable spectral data storage and retrieval system.

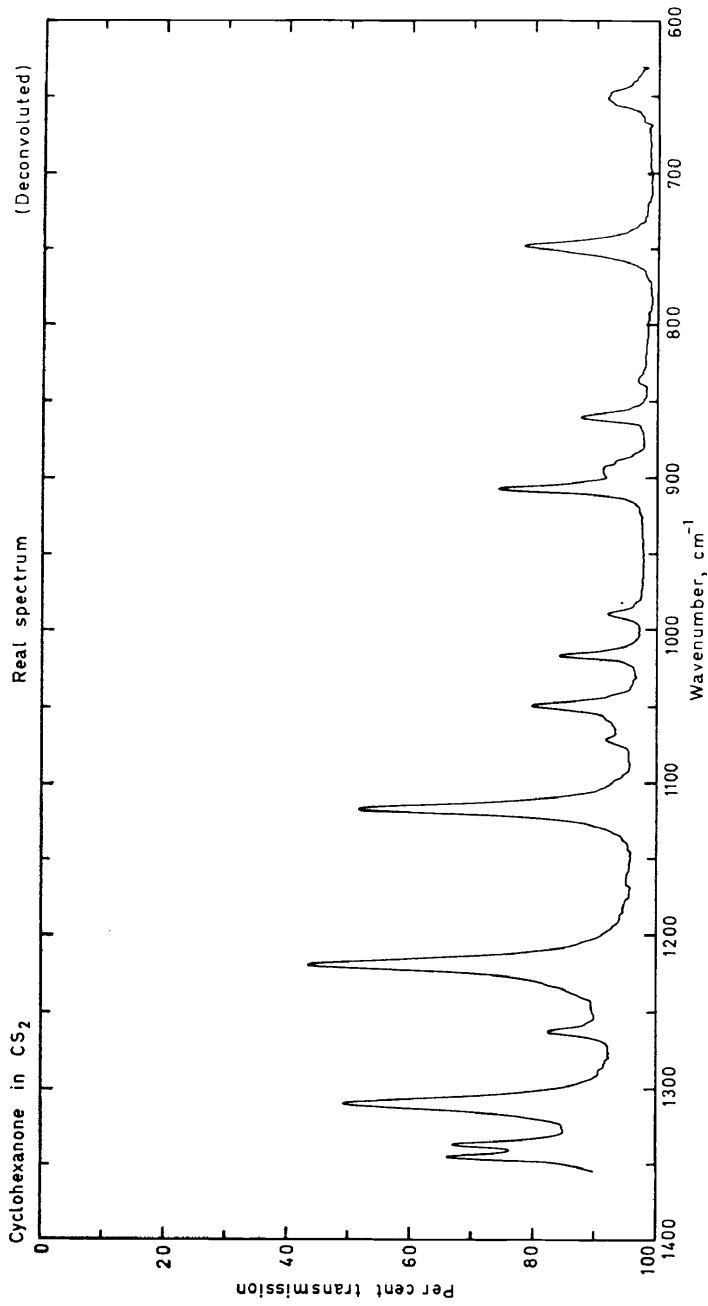


Figure 15. Computer-plotted slit-deconvoluted spectrum of cyclohexanone obtained from 1540 data points encoded at 0.5 cm^{-1} intervals.

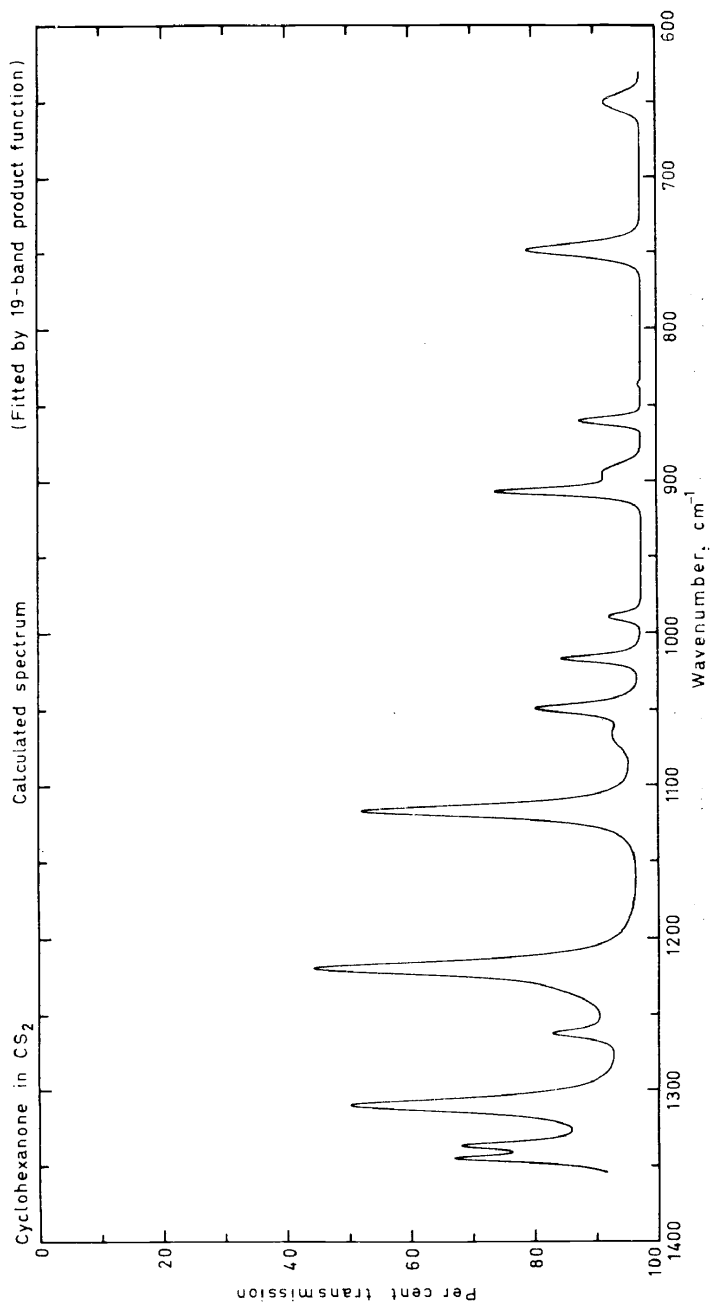


Figure 16. Computer-plotted spectrum of cyclohexanone regenerated from 77 spectral indices.

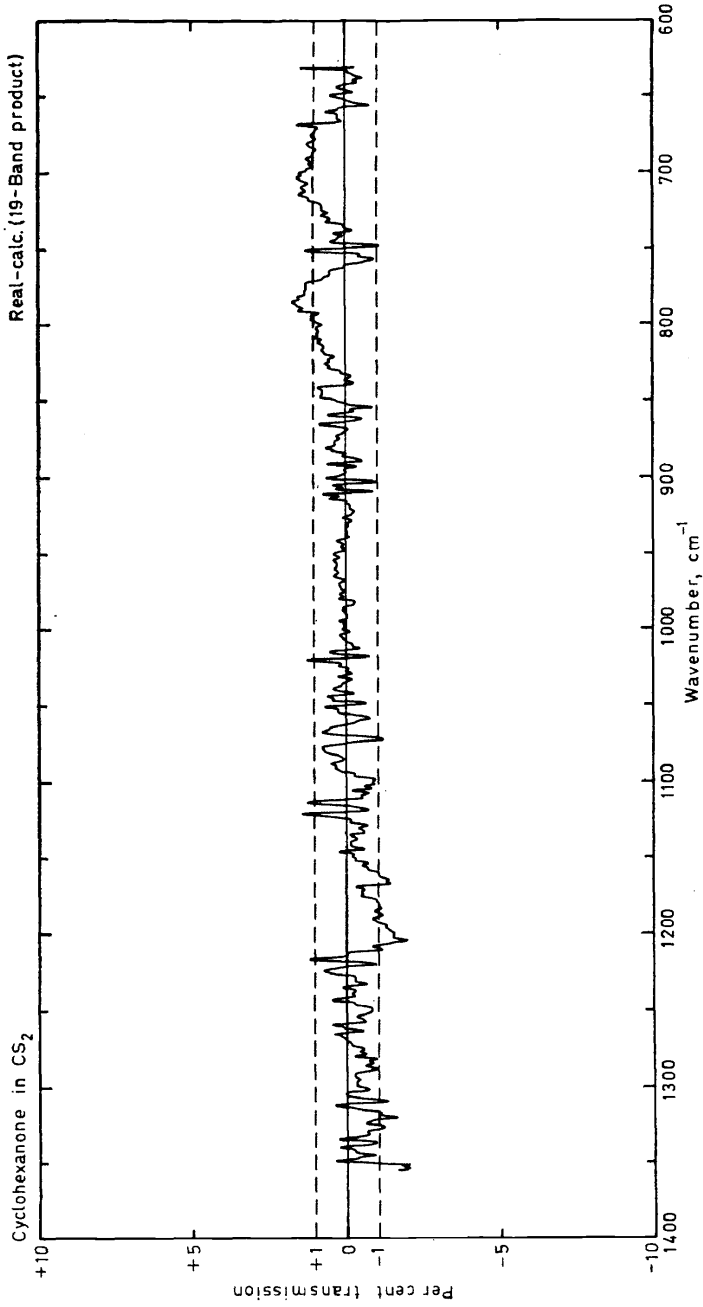


Figure 17. Error spectrum obtained by subtracting data of Figure 15 from data of Figure 16.

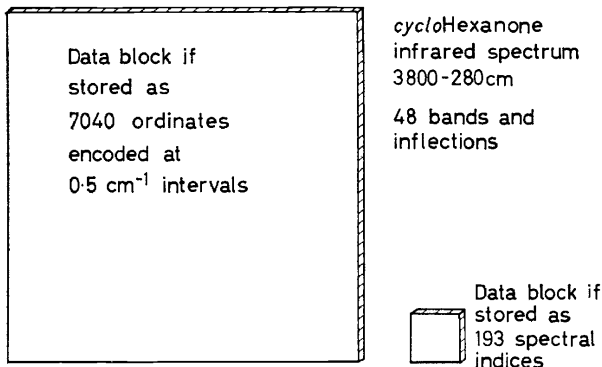


Figure 18

Several N.R.C. Postdoctoral Fellows took part in the work discussed in this lecture, and major contributions were made by H. Fuhrer, K. S. Seshadri and R. Venkataraghavan. I am also indebted to J. W. Hopkins of the Biometrics Laboratory of the N.R.C. Biosciences Division who has been our guide and mentor in numerical analysis. I also wish to thank S. D. Baxter, T. Bach, R. A. Green and T. A. Hills of the N.R.C. Computation Center, and E. R. Funke of the N.R.C. Mechanical Engineering Laboratory for their advice and help with the systems analysis and programming problems.

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