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On-Line Control, Data Collection, and Reduction for Chemical Experiments at Berkeley[1]

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ABSTRACT

A small time-shared computer system has been developed at the Department of Chemistry, University of California at Berkeley. This system is primarily aimed at control, data collection and data reduction of on-line chemical experiments. A description of the interface between the computer and our microwave spectrograph is given as an example of the kind of computer–instrument interaction possible with this system. Several results in microwave spectroscopy are given and various methods of digitally filtering the data are discussed.

The tremendous potential of using a digital computer as a control and measuring element in a chemical experiment has been known to many during the past few years. We wish to report on some of our experiences during the past three of four years, and to present some of the results of these experiments.

In 1963, Klein and Barton [1] demonstrated that by using digital averaging instead of electrical averaging in magnetic resonance experiments, it was possible to obtain data from weak absorptions which were completely inaccessible to the same instruments using a conventional strip chart recording. They also pointed out that when any instrument was pushed to its ultimate in sensitivity it would be limited by an extra component of low frequency noise whose intensity has a $1/f$ dependence rather than a uniform distribution of energy. When this $1/f$ component of noise is unimportant, the use of long time constants leads to improved signal-to-noise ratios, as shown in Curve A of Fig. 1. The signal-to-noise ratio would be proportional to the square root of the time constant. When the $1/f$ component is important, the signal-to-noise ratio approaches a maxium, as in Curve B of Fig. 1. In actual instruments, where the noise does not have an exact $1/f$ dependence, the resulting signal-to-noise ratio may even decrease with increased measur-

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[1] The experiments in microwave spectroscopy are supported by the National Science Foundation.

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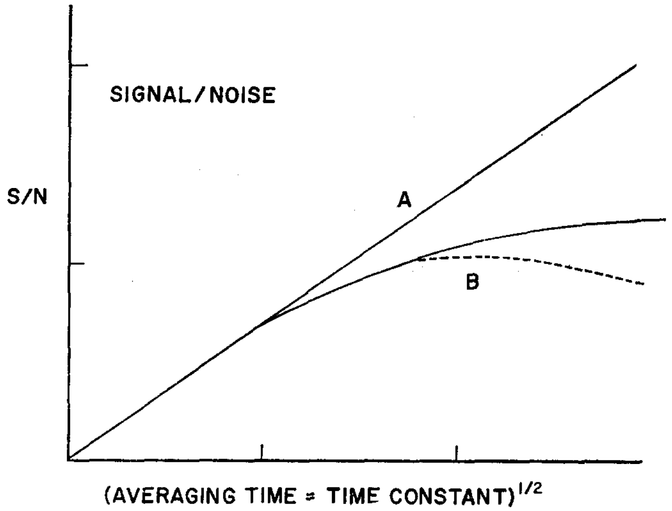

FIG. 1. Curve A shows the response of a time constant filter to noise when the $1/f$ component is not important. Curve B shows the response of a time constant filter to the actual noise present in most instruments.

ing time. The low frequency noise arises from stochastic events such as fluctuations in the power line, doors closing, elevators starting, temperature changes, etc. over which the operator has no control. This noise component is most evident as background drift in the spectrum. In most cases, instruments are constructed so as to be as insensitive as possible to these disturbances but this $1/f$ noise is usually the factor that determines the ultimate sensitivity of any instrument, when no limits are placed on averaging time. When longer time constants are used, it is necessary to sweep an experiment more and more slowly and it becomes increasingly difficult to distinguish a spectral line from these background fluctuations.

This type of noise is particularly insidious since signal-to-noise ratios are often judged by comparisons between the signal and the high-speed fluctuations. If the time constant is long enough, the output curve of a spectrometer may be perfectly smooth, yet a slight wandering of the background will shift maxima, introduce extra components, or mask real lines. The actual signal-to-noise ratio may be much lower than is often thought.

This $1/f$ component of noise limits the sensitivity of many experiments in chemistry. It is especially important for our experiments in microwave spectroscopy as well as those in electron spin resonance and nuclear magnetic resonance.

In their experiments, Klein and Barton used a pulse-height analyzer, which is little more than a small memory element of a digital computer. These experiments showed very dramatically the value of digital averaging. They replaced a single slow sweep with many fast sweeps and then averaged the multiple sweeps, by breaking up the spectra into channels and accumulating the sum of the signals for each pass in a pulse-height analyser. By this technique they were able to recover signals far below the ultimate long time constant sensitivity of their spectrometer.

It was evident that this was just a start and that the addition of the arithmetic and logic facilities of a small digital computer would greatly enhance the power of this method. There was the additional consideration that, in most large chemistry departments or industrial laboratories, there are numerous spectroscopic experiments of different types. If each were to have a pulse-height analyser, the cost would far exceed that of a small digital computer to be time shared among a number of users.

In the chemistry department there were a very impressive number of uses to which a small versatile computer could make significant contributions. Some of these are gas chromatography, infra-red and ultraviolet spectroscopy, chemical engineering process control, numerical control of machine tools in the shop, and the use of remote teletype units as desk calculators with memory. Such a calculator would be primitive as a computer, but bery sophisticated as a desk calculator, even by today's standards. Some of these uses seemed originally to be too simple to justify computer control. In a time-shared system, however, such tasks require very little memory space and a trivial amount of computer time, so it is very feasible to connect them to the computer and to make the improvement in the quality of data possible at a very low cost. In addition, the existence of a small central computer in the chemistry department would greatly enhance the computational facilities of its members. This was particularly important for many simple routine calculations which might otherwise be done on a desk calculator rather than in a large computer center, due to the long turn around time. The small central computer would allow a person more immediate access and therefore make the results more quickly available.

After about a year of negotiations, we were able to obtain a small computer. This computer was selected in early 1963 and since then there have been several new-generation computers introduced. Our particular choice of computer is possibly out of date, but some of the criteria involved in the choice are still very important. The newer equipment is faster and considerably less costly, but the possibilities of interaction with chemical experiments are very similar. The system we have is shown in Fig. 2. It can interact with experiments by the several types of signals shown in Table I. These may be yes/no signals from the computer to start or stop devices, or they may be yes/no signals from the instrument which allow the computer to test the status of that instrument. In the computer an EOM $3x_1x_2x_3x_4$ instruction generates the signal out and an SKS $3x_1x_2x_3x_4$ instruction tests an incoming signal. The SKS instruction causes the computer program to

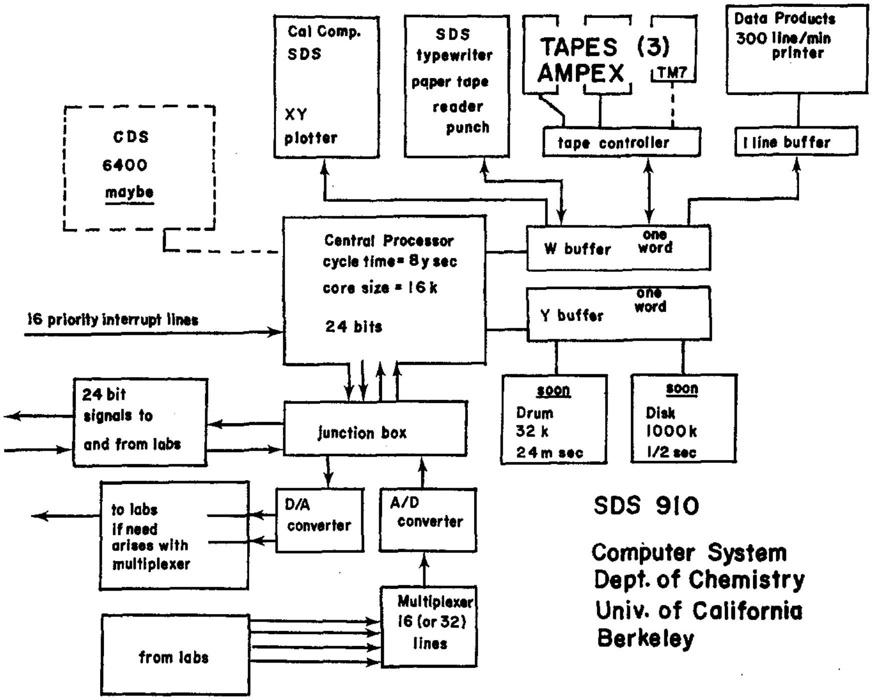

FIG. 2. The SDS 910 computer system at the Department of Chemistry, University of California, Berkeley, California.

TABLE I

SIGNALS FOR THE INTERACTION OF THE COMPUTER WITH LABORATORY EXPERIMENTS

1. EOM $3x_1x_2x_3x_4$ = 4096 control signals out
2. SKS $3x_1x_2x_3x_4$ = 4096 input signals to test
3. POT (loc) = output a 24-bit number (8 + digits)
4. PIN (loc) = input a 24-bit number
5. Read a voltage and store. ± 0.05% = 11 bits
   time required = 50 μsec if repetitive on same line
   80 μsec if set up is required
   100 μsec if one of 16 line must be selected
6. Output a voltage (2 channels)
   time = 32 μsec—(no multiplexing yet)
7. External priority interrupt. Each laboratory can force a branch to a predetermined location at the end of the current instruction.

branch one way for a yes signal and the other way for a no signal. In both cases $x_1x_2x_3x_4$ represents four octal digits. These appear as electrical signals and must be decoded outside the computer to route the signals to the proper instruments. In the future it would be well if computer manufacturers took over the task of supplying a coupler to decode and route to single lines blocks of these signals.

A second way in which the computer can interact is through a voltage. Our computer is equiped with a digital–analog converter and an analog to digital converter, so voltage is merely one of the several input output media of the computer, equivalent to cards, etc. The input line (or output line) can be selected by the computer and the incoming voltage may then be measured to an accuracy of 0.1%, in about 50 μsec (10 μsec for newer equipment). Since the signal may originate several hundred feet away, or even in another building, it may pick up stray voltages. To minimize this, voltages are always transmitted at a high signal level on the scale of -10 to $+10$ V. When low-level signals are generated in the laboratory, as from a thermocouple, etc., the voltage is first amplified to the higher range with an operational amplifier. These can be as accurate as ± 0.01%. Also to minimize stray signals, the transmission is done in a shielded twisted pair cable[3]. Our multiplexer switches both lines, and these both go to a differential amplifier of unit gain and then to the A/D converter. The differential amplifier has good common mode rejection. Although we have observed ½-V difference between the grounds of two buildings, this does not interfere with the accuracy of the measurements.

A third way the computer can interact is through digital data. For example, the output of a counter may be connected to a 24-line bus and a 24-bit number read into the computer. This number may be used directly if it is binary, but in most cases it will have to be decoded, depending on the nature of the counter. Decoding may be done easily by a computer program. Shaft encoders of any accuracy, up to 21 bits or 10^{-6} of a revolution are available for reading any shaft positions, such as found in infra-red spectrographs, etc. Linear position can also be encoded and read by the computer.

A 24-bit number can be sent out by the computer also. This can be used to set the frequency of a frequency synthesizer, to set a preset counter, to set a counter for any repeated operation, such as steps of a stepping motor. This digital information may also be used for a teletypewriter or input-output typewriter at the laboratory station.

A fourth way the computer can interact with an experiment is through a priority-interrupt system. This is the system by which a signal from the instrument requests service from the computer. We believe a priority-interrupt system is essential. In this system, a closure of a switch (transistor) at the instrument causes the computer,

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[3] Belfoil Cable #8773, Belden Wire Co., Chicago, Illinois.

if it is not working on another instrument, to branch on the next instruction to the proper independent program to service that instrument. Data is taken or sent, signals tested or sent, and on the completion of service, the computer returns to the program it was working on before the interrupt.

If an interrupt is being serviced at the time of a second interrupt, the computer is taken over immediately if the second interrupt is higher in priority. If the priority is lower, the second instrument must wait for the high interrupt to be finished. High priorities are assigned to fast experiments which will lose data if it is not taken immediately, and low priorities to experiments that will not lose data if forced to wait. The slowest experiment should not have to wait more than 10 msec. We have reserved the highest-priority interrupt for an emergency interrupt if a slow instrument has waited a long time and is about to lose data. To date, it has not been necessary to use this emergency interrupt.

The lowest priority is assigned to a panel switch. This allows the operator to gain control over a background program (no priority) but not over on-line instruments.

The fourth-lowest interrupt used is a digital clock. Pulses, at 100 or 1000 cycles per second from one of the frequency standards[4], at the microwave spectrograph initiates this interrupt. At present this is wired as a single instruction interrupt which increments a location in core. Reading this number gives the time. This clocked interrupt will probably be changed in the future to also do anything that requires periodic service.

The time in high-level interrupts is limited to about 1msec, so instruments with low level interrupts can always be serviced. In the higher interrupts, data and signals are taken in or sent out and then the priority is released. When there is a need to work up the data or do much arithmetic, a program address is put in a queue and an EOM signal is sent out which trips the second-lowest priority interrupt. The data is then worked up with priority over a background program or operator intervention, but not over other instruments.

There are two systems which may be considered a substitute for a priority-interrupt system. They use a single interrupt line. In one case this is tripped by any device needing service. Then an executive or monitor system makes various logical tests to find which instrument needs service. In the other system a clock periodically trips the interrupt and the program tests whether any instrument needs service. These systems are adequate for slow experiments but carry a very high overhead in both computer time and programming space. We considered such systems to be too cumbersome and inflexible for our purpose and we placed great importance on a priority interrupt system where each instrument or type of instrument is handled separately by short resident programs in the computer. Long

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[4] Model 100E, Hewlitt Packard Corp., Palo Alto, California,

data-reduction programs are brought from peripheral storage under the second lowest priority interrupt.

There is one other feature of computers which is very important for on-line use. Often if the computer is given an instruction to take in data from an external device, it is completely tied up until that data arrives. It is therefore essential that input/output buffers or data channels be used with interrupts so that the central processor is never tied up waiting for data. It is also highly desirable to have interlace registers and provision that the data channel be able to communicate directly with core. An interlace register contains a word-count register and beginning address register. These are set in two or three machine instructions and the data transfer is handled between the core and data channel.

An example of the importance of interlaced data channels may be seen by a description of how a line is printed on our line printer. This takes 200 msec. The central process uses about five instructions for tests and paper advance, then in two instructions sets up the buffer and interlace register. The central processor has completed its function and now the buffer and core transfer data to a one-line core buffer in the printer. This is done by using two machine cycles out of every twelve for data transfer. This requires 3 msec and during this time the computer is always free to service an interrupt from an instrument in the laboratory. If an interrupt comes during the data transfer, the computer services the instrument during 10 out of every 12 machine cycles. During the rest of the print time of 197 msec, the computer is completely free. Magnetic tapes use a longer transfer time but a lower percentage of machine cycles. As a result, the computer is always ready to service an interrupt from an instrument in some laboratory. At times the computer has been in use on-line to the microwave spectrograph or infra-red spectrograph while the tape units were being tested. The tape units were going at full speed, alternately reading from one and writing on the other. In between, data was being printed. Occasionally the computer was interrupted from the keyboard to change the tape test. The on-line digital control and measurement of the microwave and infra red spectrographs continued without interference.

There is one other item of computer equipment which is very valuable. This is a drum or fixed-head disk for peripheral storage of data. Many relatively inexpensive models have become available recently. We have been modernizing an old surplus drum but it is not yet useable. With a spectrograph taking 2000 to 3000 points of data, the bulk data would be stored on the drum and only a buffer of 50 working spaces in core would be used for data storage. When the 50-word buffer is filled, it would be transferred to the drum and the old data for the next 50 channels would be brought in to core for the next 50 measurements. This greatly reduces the core requirement for most on-line experiments.

Several instruments are connected to the computer. Figure 3 shows an early NMR spectra taken with a very simple interface. The bottom three curves are

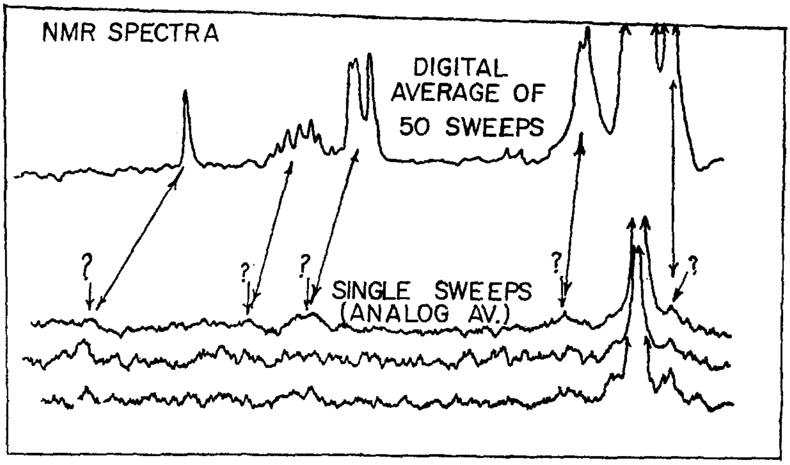

FIG. 3. An early NMR spectrum showing the advantages of digital averaging to recover signals buried in noise.

conventional scans at the sensitivity limit of the instrument. The top curve is the average of 50 such scans. The frequency scale is different in the computer output, so arrows have been drawn to show equivalent positions. Recently, the NMR spectrograph has been connected to the computer with a new interface by Wilson and Sternlicht. Also, Paukert and Johnston have connected an infra-red spectrograph to the computer and use it routinely in their studies of free radicals.

As an example of what has been done with computer–instrument interactions, we have chosen the microwave spectrograph. Here absorption coefficients are very small and often much fundamental chemical information is contained in lines with absorption coefficients as small as 10^{-11} cm^{-1}, or less. Under optimal operating conditions of a ten-ft absorption cell and about 1 mw of incident power, these weak signals represent absorptions of only 10^{-12} W, in the presence of 1 mW background. These are beyond the limits of sensitivity using conventional recording techniques. In an effort to retrieve these weak signals, we have connected our microwave spectrograph to the computer. In this interface we have tried to exploit as many as possible of the advantages of computer–instrument interaction. Because of the competition for time and energy between development of the interface and studies of molecular structure, many possibilities remain untried. Some of these that have been tried allow for direct control of the spectrometer by the computer, simultaneous compatibility with other experiments and calculations, immediate output of the results from the computer to the laboratory, considerable flexibility as to the course of the experiment under operator control and the possibility of simultaneous data reduction.

A block diagram of this interface is shown in Fig. 4. At the center of this system is a Montronics Model 304A frequency synthesizer. This instrument is capable of producing, by direct synthesis from a 1-MHz quartz crystal, any frequency from 1-Hz to 11-MHz in 1-Hz increments with a stability of a few parts in 10^9. Any frequency in this range can be selected remotely by applying the proper voltages to transistor gates in the rear of the instrument, and the switching between any two such frequencies can be accomplished in about 1 msec or less. When these gates are driven by the parallel output bus of the computer, this provides a direct means of controlling frequency. It was necessary however to construct a programmer which could convert the BCD data of the computer into a 10-line decimal format required by the switching lines of the synthesizer. This programmer also served as a buffer register between the computer and synthesizer, and provided the necessary digital storage of the frequency during the period of measurement. This allowed the computer to disconnect from the microwave spectrometer after once setting the frequency, and it could then return to its prior operations without having to remain idle during the entire measurement.

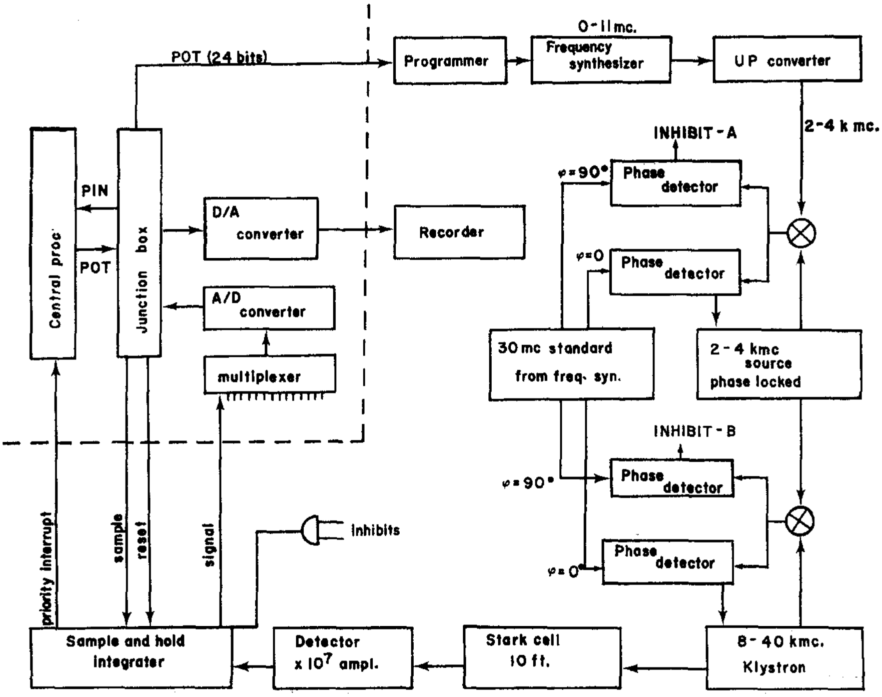

FIG. 4. The interface of the microwave spectrometer to the SDS 910 computer.

Microwave spectroscopy, however, is concerned with considerably higher frequencies in the range of 8–40 Gc and the fundamental frequency of the synthesizer was multiplied up to this range using a series of phase locked oscillators. Since frequency increments from the synthesizer were discrete rather than continuous, and switching was accomplished with a random phase shift, the higher frequency oscillators often momentarily lost their phase lock on switching. It was necessary, therefore, to introduce means of testing the status of all the phase-locked loops and to inhibit the measurement cycle until all the oscillators returned to stabilization. This was accomplished by introducing a phase detector in quadrature to each loop. This produces a positive voltage for each loop while stabilized and zero volts when the loop is no longer stabilized. The measuring cycle is inhibited until this signal is above a certain threshold.

Since the spectrometer remains at a specified stable frequency during the period of measurement, no simple time-constant filter can be efficiently used to average the signal. If time constants which are comparable to the measurement time are used, the signal does not reach its maximum, as illustrated in curve B of Fig. 5. Considerable distortion will be introduced into the measurement. In addition, transients introduced by the digital switching may seriously interfere with the measurements because of their long persistence. On the other hand, when time constants which are small compared to the measurement time are used, the signal is allowed to reach its maximum value, but only a small fraction of the time is spent averaging the signal. This case is illustrated in curve C of Fig. 5. In order to circumvent these difficulties, a sample and hold integrator[5] which could be reset to zero was developed to replace the conventional time-constant filter.

The combination of a short time constant and integration allows for fast response and accurate reading along with efficient use of instrument time by averaging over the entire measuring cycle. The fast response also allows switching transients to die out before the measuring cycle is started. This behavior is represented as curve D in Fig. 5.

Let us now illustrate the system by considering a typical measurement cycle. The computer first generates the desired spectrometer frequency and transfers this data to the synthesizer via the programmer. The computer now disconnects from the microwave apparatus and continues its duties with other experiments and calculations. The synthesizer frequency is multiplied up to the spectrometer source by the phase-locked oscillators. When all phase locks have stabilized, as indicated by the quadrature phase detectors, integration of the spectrometer signal for that frequency is initiated and continued for a specified period of time (usually 0.1 sec to 1 sec). If any of the phase locks are disturbed during the measurement, the

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[5] This device is now commercially available from Burr-Brown Corp., Tucson, Arizona. It is called a three-modes integrator # 4003/16.

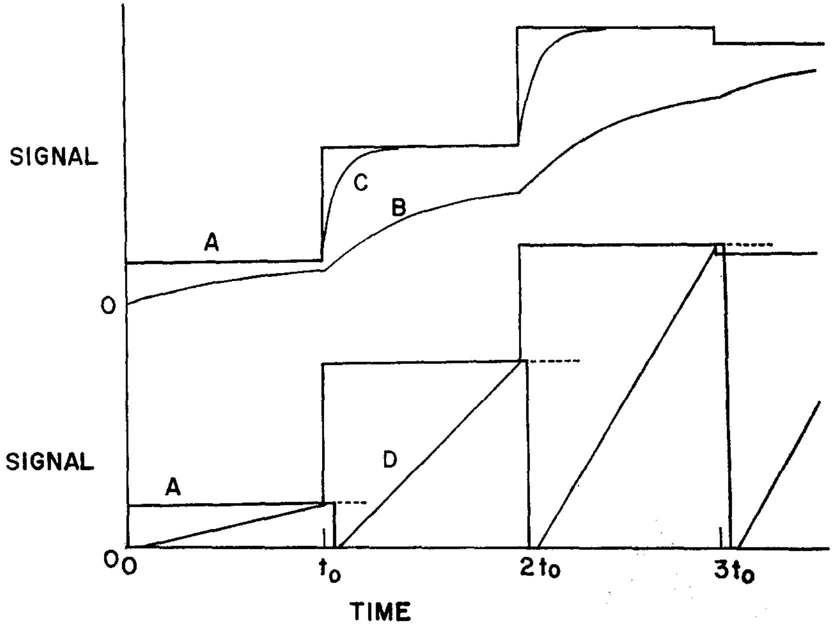

FIG. 5. The operation of a sample and hold integrator compared to filtering with a resistor and capacitor: Curve A is the signal without noise; Curve B is the signal when averaged with a time constant, $\tau = t_0$; Curve C when $\tau = t_0/10$; and Curve D is the output of the sample-and-hold integrator. Note that Curves C and D give the correct output signal but that Curve D averages over entire time, whereas in Curve C the average is only over 10–20% of the time.

integrator is automatically reset to zero until stabilization occurs, at which point the measurement is initiated again. At the conclusion of the measurement, the integration is terminated and the voltage corresponding to that frequency is held until read by the computer. A priority interrupt is immediately sent to the computer to signify that a successful measurement has been made and to initiate service of the microwave spectrometer again. If perhaps the computer is in use by an experiment with a higher priority, the entire system remains idle without losing its data. The computer, when available, reads the voltage using the multiplexer and A/D converter, resets the integrator to zero to await the next measurement, generates the new frequency desired and then disconnects again. This process is repeated until the specified number of scans over the given spectral region is completed. The record may then be returned, under operator control, by the D/A converter to the laboratory for examination, and may be stored on magnetic or paper tape for future reference.

This interface illustrates many of the advantages of a computer-coupled experiment over conventional recording techniques and also contains several unique features which facilitate the collection and treatment of data.

Of particular importance was the establishment of an effective and efficient means of performing digital averaging of many successive scans. Since the frequency of the spectrometer is controlled directly from the computer to within a few parts in 10^9, all scatter in the frequency axis is completely removed and an absolute channel registration is established. This guaranteed that many successive scans could be summed digitally without introducing any errors from spectrometer frequency drift, and all uncertainties in measurement would result from noise or uncertainties in voltage. Figure 6 shows a weak microwave signal observed using conventional techniques. Under the given operating conditions, it represents about the best obtainable with time-constant filtering, and yet it contains considerable low-frequency distortions and fluctuations. Figure 7 shows the same line taken digitally using equal-time and identical instrument conditions except that the stark modulation voltage and frequency scales for the two records are different. Digital filtering as described later was also used.

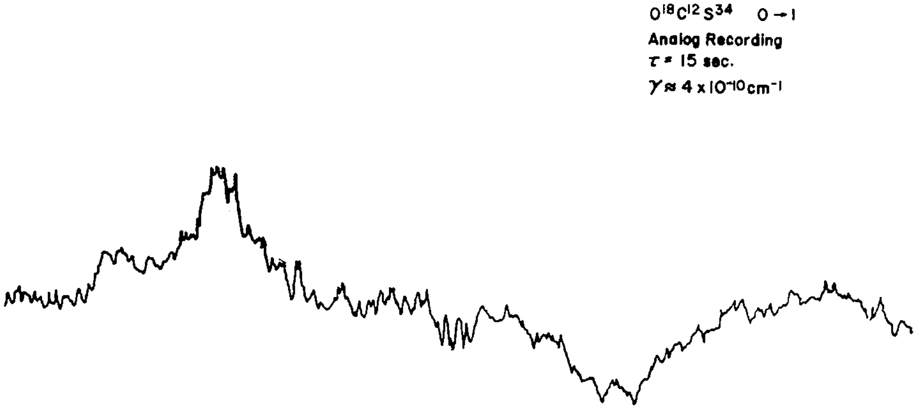

FIG. 6. Microwave spectrum of ^{18}O, ^{12}C, ^{34}S 0–1 transition obtained using a conventional analog recording with a time constant of 15 sec.

Figures 8–10 show how this signal builds up under successive scans and digital averaging. It can be seen that much of the phase coherence of the low frequency noise has been removed. Since the only limit on ultimate sensitivity is the operator's patience, the signal-to-noise (s/n) ratio can be increased over that in Fig. 7 if desired by summing even more scans. The experiment was stopped at this time only to demonstrate what could be gained by using digital techniques at no expense in time.

A further result of the digital sweep is that very little time is spent between

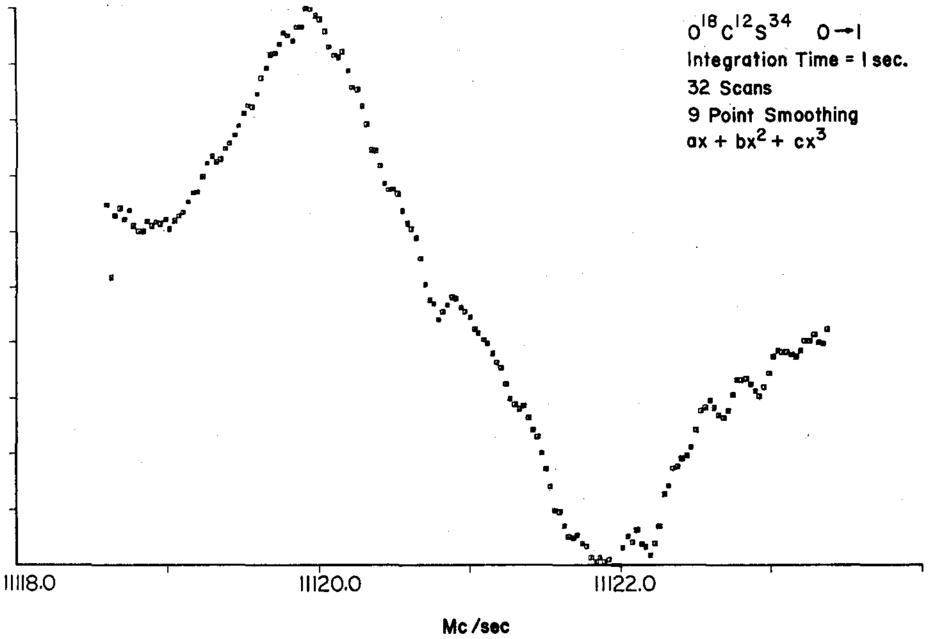

FIG. 7. Microwave spectrum of $O^{18}C^{12}S^{34}$ 0–1 transition obtained by digitally averaging 32 sweeps. Computer filtering was also employed. This figure should be contrasted with Fig. 6 which represents about equal averaging time but using conventional techniques.

measurements, only a few milliseconds for each point are required for the computer to service the microwave spectrometer and for the frequency to change. In contrast to continuous sweeps, this represents an extremely efficient use of the spectrometer [illegible] spectral region. For example, if there are only a few points per line width, a spectral search can be initiated that is about 10–20 times faster than conventional methods with the same sensitivity. This is apparent since a conventional continuous search must treat all frequencies identically, while in the digital search no time is spent between the widely spaced frequencies. The search can be continued by repetitive scanning until a few points are statistically removed from the noise and indicate the presence of an absorption. A new sweep pattern with a higher density of points can then be introduced over the areas where lines are indicated in order to develop a record of the shape, position and intensity of the absorptions.

The necessary compatibility of the microwave system with other experiments and calculations for a time-shared mode of operation is ensured in several ways. Frequency sweep is controlled directly by and in response to the computer. In addition, the voltage representing a successful measurement is held, without detectable drift, by the sample and hold integrator for about 100 msec after the completion of the measurement, or until read by the computer. If the signal is not read by the computer in this time, the measurement is invalidated and the integration is repeated. These two facts guarantee that, no matter how heavy the computer use and how slow the response is to initiation by the spectrometer, due to higher priorities in use, no data is lost and no false measurements allowed. The spectrometer, during such periods, however, remains idle. To date there has not been any detectable delay in service by the computer. Secondly, only a small fraction of the total computer time (about 0,5 %) is required to service the microwave spectrometer. This permits many other experiments and calculations simultaneous access to the computer.

As yet, nothing has been said about the computational facilities of the computer for data reduction, and we now wish to discuss these and show some examples. In general, simple absorption spectra are obtained in microwave spectroscopy. The measurement of the average voltage at each frequency is completely independent of the measurement at any other frequency. Still there exists a relationship between

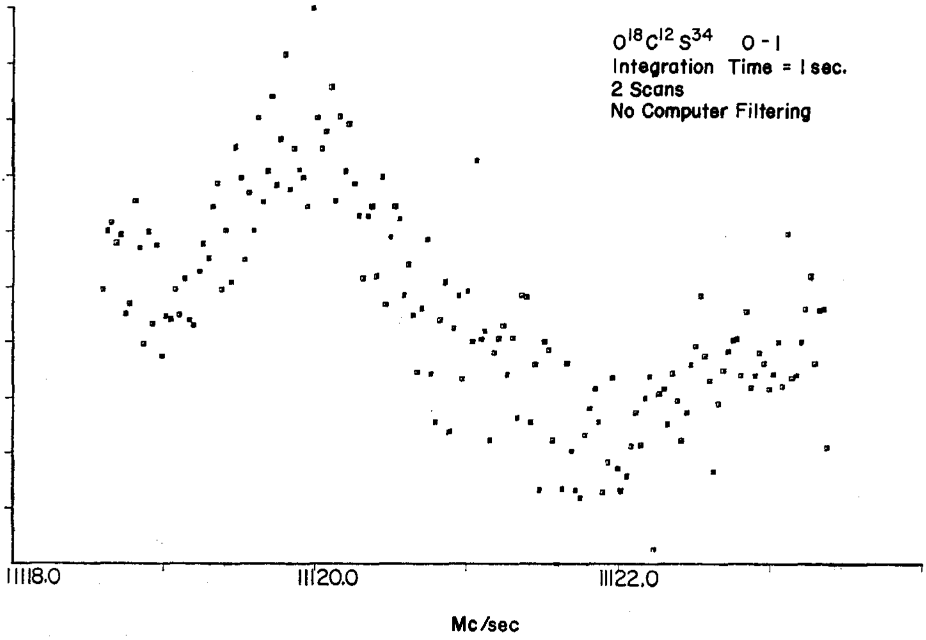

FIG. 8. Microwave spectrum of $O^{18}C^{12}S^{34}$ 0–1 transition obtained by digitally averaging 2 sweeps.

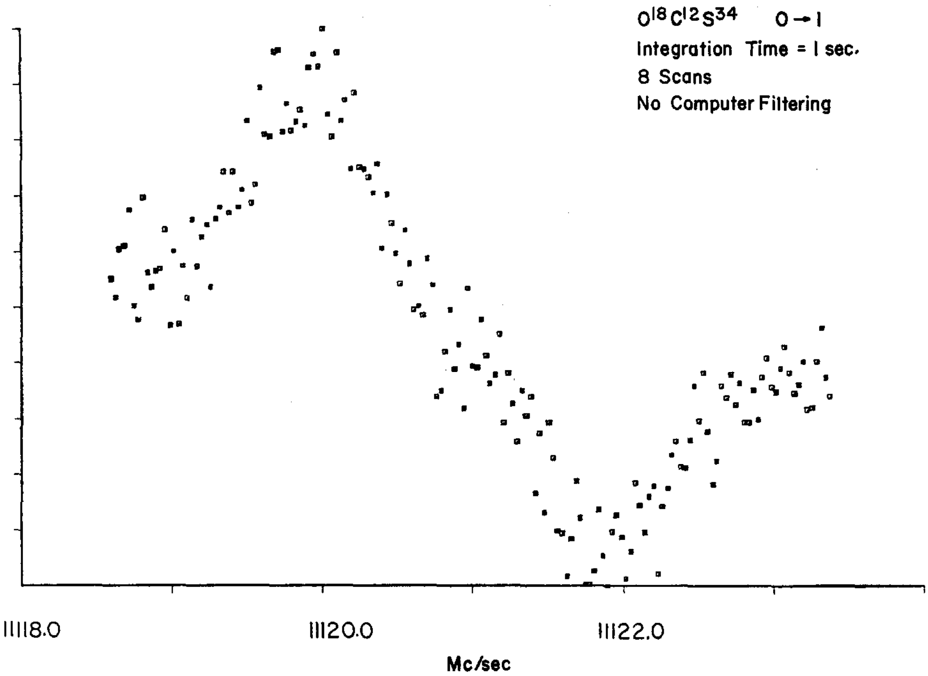

FIG. 9. Microwave spectrum of $O^{18}C^{12}S^{34}$ 0–1 transition obtained by digitally averaging 8 sweeps.

the absorptions at various frequencies. This correlation between points may be exploited in several ways. Two methods have been particularly useful.

The first method is very simple to apply and it gives an immediate assessment of the data. It is particularly useful for feedback to the operator during the course of the experiment. It assumes only that adjacent points are correlated to give some smooth curve. This is the method introduced by Savitsky and Golay [2] and assumes no prior knowledge of the shape of the line or multiplet other than the spectra must be smooth and without excessive curvature.

Although one may simulate any type of filter in the computer, probably the best consists of finding the optimum fit, in a least-square sense, of a general polynomial function of the form $y = a_0 + a_1x + a_2x^2 + a_3x^3$... to a limited number of successive data points. This function is the best simple smooth curve which represents the data in this small region of the spectrum. Values at the center frequency in this region may be calculated from this expansion and preserved as one point on the smoothed curve. One may then shift the frequency region slightly by adding the next successive point on one end and dropping the last one from the other end.

The fitting procedure can then be reapplied to this new region, center value calculated, and added to the filtered curve. By moving throughout the spectrum in this manner, the smoothed spectrum is obtained. Savitsky and Golay have shown that if the data points are at uniformly spaced intervals, this technique, for low order polynomials, is equivalent to a simple convolution procedure involving fixed weighting factors. The computer program for the smoothing is very simple and it is feasible to use it during the data-collection period.

In smoothing, as in time averaging, the noise is reduced by approximately the square root of the number of data points in the smoothing interval. However the intervals must be limited to a moderately small fraction of a line width; otherwise significant features of the spectra are smoothed or distorted. Higher densities of data points allow the use of more points but decrease the total number of repetitive scans that can be accomplished in a given amount of spectrometer time. Thus the final configuration of density of points, number of scans, and size of smoothing interval must reflect a compromise based on the character of the spectra and nature of the information to be obtained. In general, we have found that intervals on the order of 9–13 points are most convenient and polynomials that include up through cubic forms represent the best smoothing function [3]. If higher-order polynomials are used, it has been found that single fluctuations tend to be fit.

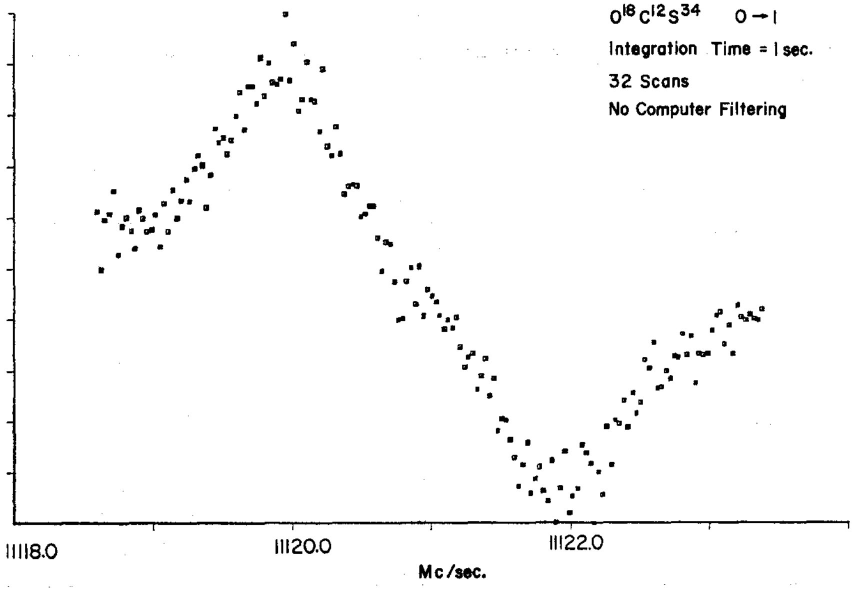

FIG. 10. Microwave spectrum of $O^{18}C^{12}S^{34}$ 0–1 transition obtained by digitally averaging 32 sweeps.

This computer filter has three significant advantages over any real experimental filter. The first of these is that the unfiltered numerical data from each experiment is saved and at any time an optimimum filter may be selected. In this post filtering of the data, both the interval size and degree of polynomial used may be varied until the best results are obtained. In contrast, for an electronic filter, the experiment must be repeated if the filter conditions are not satisfactory. The second great advantage is that the computer filters in the frequency domain, whereas the electronic filter is in the time domain. The electronics cannot anticipate the future and depend only on the past frequency points. The digital filters are symmetrical in frequency and introduce little distortion and no asymmetry, whereas the electronic filter distorts the spectral line toward those frequencies measured last. As a result, with electronic filters we always sweep through the line in both directions and average the position of the peak in order to determine the frequency of an absorption. We gain nothing in signal noise ratio by this extra measuring time but it is necessary to correct for the asymmetry of the electronic filter. A third advantage is that a single large fluctuation causes only a very small disturbance when a digital filter is used, whereas a single large noise spike in an electronic filter creates a disturbance which persists for a long time (several time constants).

The results of smoothing can be seen in Figs. 11 and 12. In Figure 11 the data barely suggests the presence of an absorption, while in Figure 12 the smoothed data clearly indicates an absorption. This is further demonstrated by Fig. 7, which shows the smoothed data of Fig. 10. This should also be contrasted with Fig. 6 showing the same signal under similar conditions but obtained by a conventional time constant recording. Figures 6 and 7 represent the same averaging time and clearly indicate the more efficient use of instrument time using digital techniques. In the analog recording the time constant was 15 sec. This time constant is equivalent to 30 digital integration times of 1 sec each because with analog filtering it is necessary to sweep the spectrum in both directions to make a frequency determination.

It should also be noted that the data of Fig. 7–10 were obtained while time-sharing the computer with an infra red spectrometer and with the testing of the magnetic tapes. There was no interference.

As illustrated in Fig. 7 and 12, some low-frequency noise remains, even after computer filtering. This is an indication that the phase coherence of the noise is not completely random under the given operating conditions. One reason for this could be that linear frequency sweeps have been used, and this contains an element of regularity which would allow some phase coherence in the noise. As pointed out by Professor Martin Graham,[6] this phase coherence could be further decreased by employing a random sweep pattern. Although this capability exists with our

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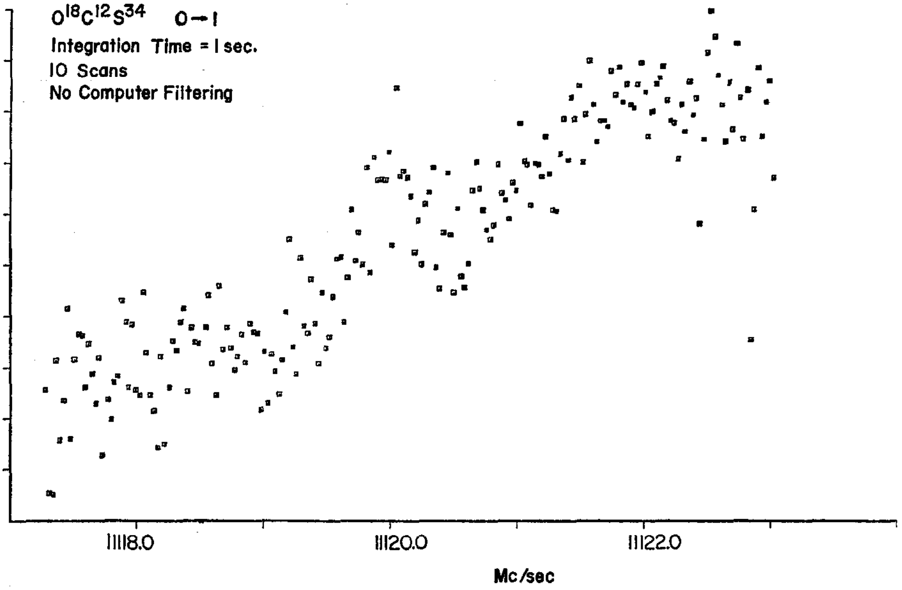

FIG. 11. Microwave spectrum of $O^{18}C^{12}S^{34}$ 0–1 transition obtained by digitally averaging 10 sweeps. The conditions were not as favorable as in the preceding Figures. No computer filtering has been used and the presence of an absorption is not definite.

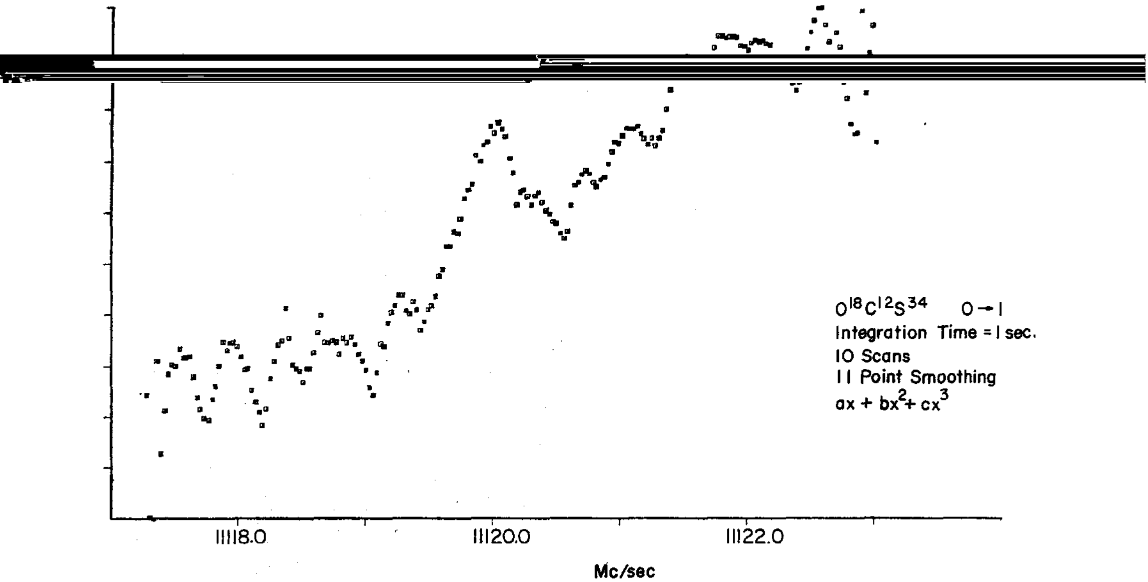

FIG. 12. The data of Fig. 11 has been computer filtered by digital smoothing and clearly indicates an absorption.

frequency-synthesizer system, it represents several experimental difficulties, and we are presently solving these in order to use a random, or semirandom, sweep.

Often the spectral record consists of superimposed lines which are not completely resolved. It has been shown [4] that these lines may be effectively narrowed by convolution techniques similar to those used in smoothing. This consists in subtracting a certain fraction of the second derivatives of the absorption from the absorption and yields lines with about $\frac{3}{4}$ the original half-width. The resultant narrowed lines, however, no longer have the characteristic Gaussian or Lorantzian shape, but rather contain considerable reduced intensity in the tails. This also enhances resolution. This technique is illustrated in Figs. 13–15. Figure 13 shows a doublet consisting of the ground and an excited vibrational state in 1,1-difluorocyclobutane. It was obtained using conventional recording techniques under typical operating conditions. Using the computer for digital averaging, it was possible to improve the sensitivity enough so that the operating conditions could be optimized to resolve the two peaks. By lowering the sample pressure and the incident klystron power, the pressure broadening and saturation broadening were reduced to a point where the barely-discoverable shoulder of Fig. 13 was

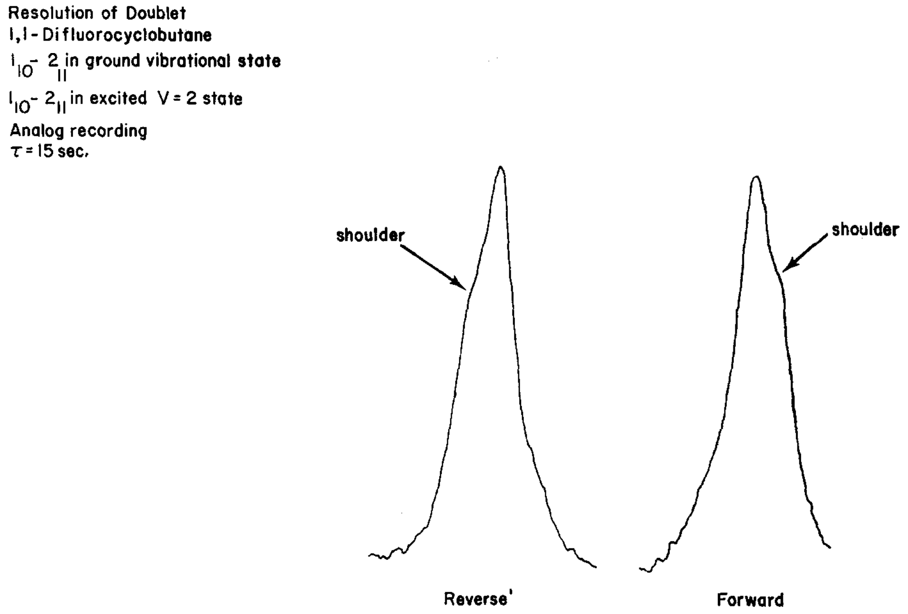

FIG. 13. A doublet consisting of the ground vibrational state and the excited $V = 2$ state of 1,1-difluorocyclobutane as indicated by the shoulder on the main peak. The spectrum was obtained under typical operating conditions using an analog recording and a 15-sec. time constant.

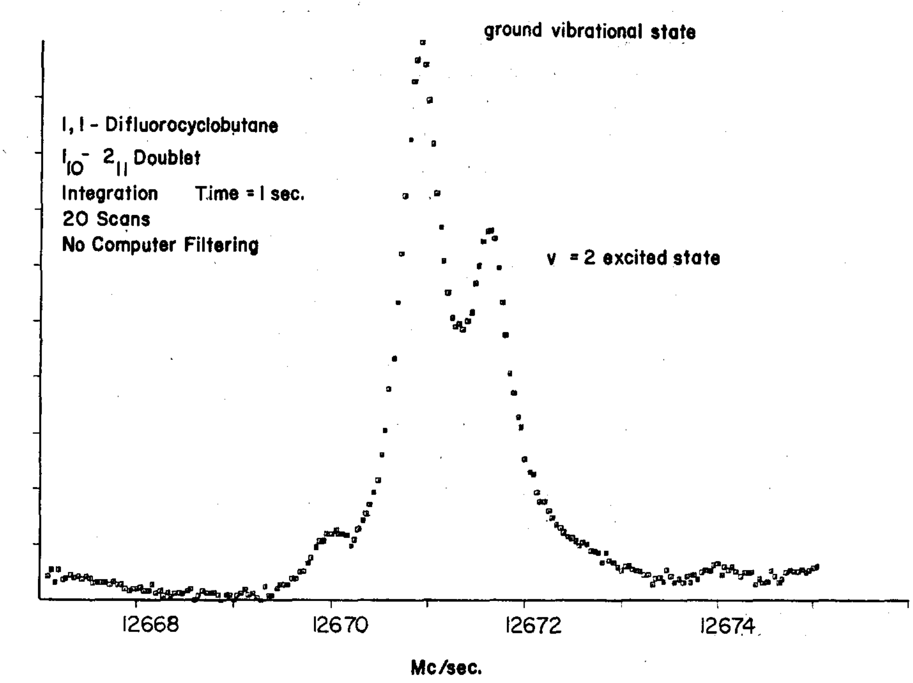

FIG. 14. The doublet of Fig. 13 which has been partially resolved by digitally averaging 20 sweeps. The enhanced sensitivity of the digital techniques allows the operating conditions, i.e., sample pressure and incident power, to be optimised for resolution.

partially resolved, as shown in Fig. 14. The two lines were completely resolved using the digital narrowing techniques discussed above, as shown in Fig. 15. It can be seen from this figure that the curve-narrowing process does introduce a certain amount of noise. The resolution of these lines was a key factor in the final interpretation of the spectra of this compound.

All of the basic information in the spectra is contained in the raw data, and these convolution techniques cannot be used to create new information. To a certain extent they allow one to trade off and emphasize certain aspects of the spectral information at the expense of others. For example, smoothing represents a gain in sensitivity while reducing resolution, and in resolution enhancement, the converse is true. These techniques are particularly important for visual examination and allow the operator to gain insight into what information is contained in the spectra, such as whether a weak line exists or whether a line is a doublet. However, what is generally desired is the spectroscopic parameters, i.e., half-widths, intensities and positions of all the lines.

In most fields of spectroscopy the investigator has considerable knowledge of line shapes. The second method of digital filtering involves the introduction of a standard line shape, depending upon as many parameters as desired. In microwave spectroscopy we use a Lorentz curve with the position, height and width as parameters, and usually only a common width is used. Least squares is then used to obtain the best fit to the experimental data. This method is most useful for extracting the final spectroscopic parameters from the data.

An example of this is shown in Fig. 16, where the doublet of Fig. 14 is fit to two independent Lorentzians. The unsmoothed data was used. Although these parameters may be determined by visual observation of the spectra, considerably more accuracy is obtained by the fitting procedure.

The striking success of these methods is in part due to spectroscopists not using all of their data. Traditionally we use from 25 to 50 time constants to measure a line, since serious distortion results if less are used. We then, by eye, average two or three time constants near the peak and select the center frequency. The digital technique uses all 25 to 50 points. Some of these are not very sensitive to the

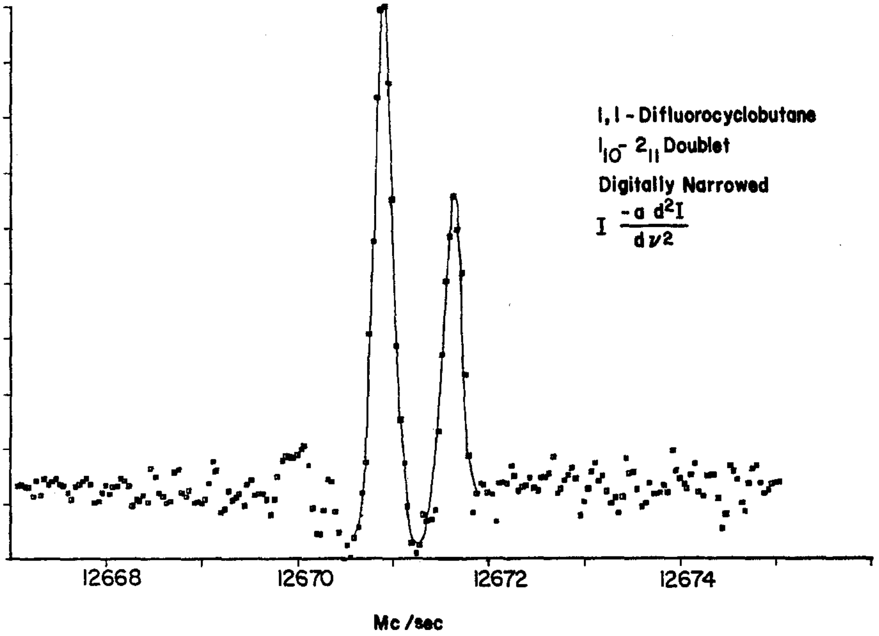

FIG. 15. The data of Fig. 14 with the absorptions digitally narrowed by subtracting out some second derivative of the absorption. The line connecting the data points is drawn by hand to show the shape and complete resolution of the two lines.

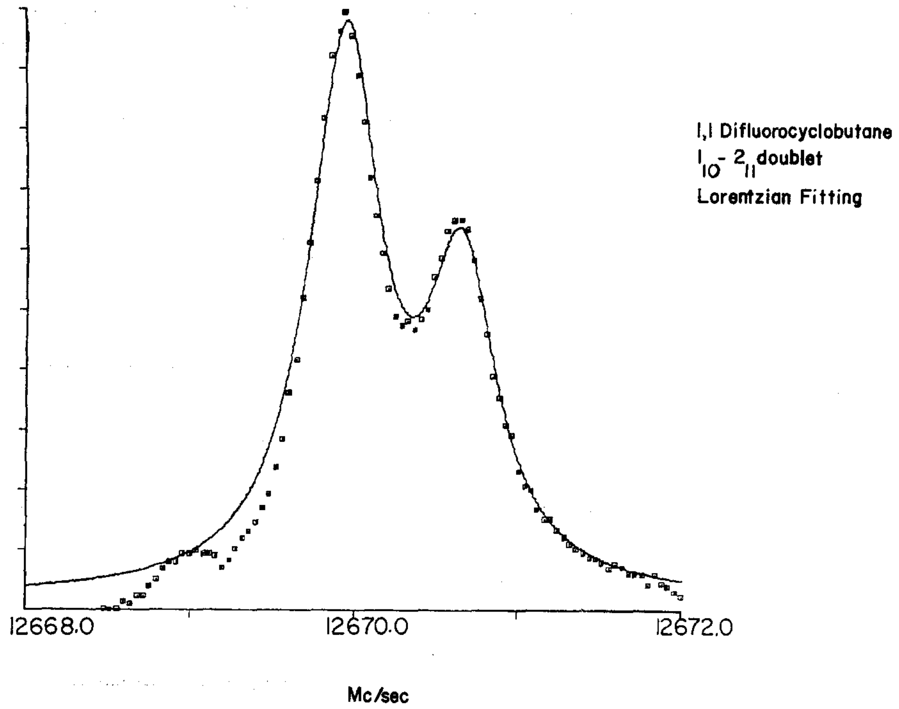

FIG. 16. Least-squares fitting of two Lorentzian curves to the data of Fig. 14. A common line-width was used for both.

position of the line, but the ones in the side of the line are better to use for the determination of the center frequency than the usual ones near the peak. This is also true for the resolution of multiplets. By using all of the data in digital techniques an improvement of a factor of about 4 or 5 should be expected. Some additional improvement arises because the spectra is measured at fixed points in frequency rather than over a range of frequency.

The power of using all the available data has also been shown by Keller, Lusebrink and Sederholm [5]. In spectra where the line-width is instrumentally limited, they fit *n* lines to a multiplet spectrum, using least-squares techniques where *n* is given successively higher values until the least-squares residual no longer decreases significantly. The agreement between the frequency and number of resolved lines and those calculated from a small number of coupling constants is very striking. Another good example of using all of one's data is the analysis of digital data from electron spin resonance by Bauder and Myers [6]. Here the experimental points are related directly to coupling constants and concentration of species, with very significant improvement over conventional techniques. In a similar manner, much of the success of Fourier transform spectroscopy is that the spectroscopist cannot see his spectrum until he makes a Fourier transform and consequently must make use of all of his data.

A new spectrograph is now under construction. It is a low frequency spectrograph, intended for the observation of free radicals. We are especially interested in some transient effects of OH. In connection with the interstellar 1665-mHz maser of OH we have predicted that the reaction

$$H(\sim 6eV) + H_2O = H + H + OH$$

will produce OH in a specific set of quantum states. The OH is then to rapidly radiate its excess energy and preferentially populate certain hyperfine levels of the ground-state multiplet. We wish to observe whether this is true and if so to determine the rate of thermal equilibration. We also wish to search for free radicals such as CH. To do this, we plan to use a very short and moderate pulse of energy to form the radicals. Several groups have unsuccessfully tried to find these radicals, but they had no way to average several experiments and they used very large pulses. Their spectrograph did not recover from the disturbance in a sufficiently short time to see the radicals. By using smaller pulses and computer averaging, we have a better chance of seeing these short-lived species. We may average 100 to 1000 experiments per second and it is possible to continue several hours or more in order to build up an adequate signal. In order to observe transient phenomena, the computer will read the output of the spectrograph on every half cycle of the Zeeman or Stark modulation. The modulation shifts the frequency of the absorption and effectively gives a measurement of the empty cell. A 5-Kc modulation frequency is used so readings will be taken at a rate of 5000/sec on the empty cell and 5000/sec on the cell and sample. After each energizing pulse, the cell will be measured for about 20 modulation cycles. For many pulses these 20 measurements will be averaged both together and separately. All of the available observation time will be used to find the line. After the line is found, the separate 20 averages will be calculated to give the time dependence of the line. This experiment would be assigned a high-priority interrupt which it would hold for several milliseconds (longer than standard for the system) but it would leave an equal time interval between experiments so that slow systems could continue to operate with no interference.

The new spectrograph is also being set up with a frequency-control system with the computer in the control loop. Low-frequency klystrons (frequency sources) are quite stable for 0.01 sec or less and frequency counters are available to count them directly. Their frequency may be shifted by the variation of a voltage. Every 10 msec, the counter will count the frequency and it will be read into the computer. The computer will find the error in the frequency, or the frequency shift required to reach the next point. It will then calculate the error voltage from the slope and curvature of the voltage–frequency curve and send the error voltage back through the D/A channel. The klystron-frequency-sensitive element, the reflector, is controlled by a conventional power supply and a sample-and-hold amplifier. The amplifier is taken off hold as the error voltage is added to the power-supply voltage and then is placed back on hold with the klystron jumping to the correct frequency. Initially the derivative of the voltage frequency curve would be given as input data, but after a few corrections the computer would recalculate the actual derivative and curvature and would continuously update these values so as to always make the proper corrections.

In the search for free radicals such as CH several of the features of the operating computer system described above will be particularly valuable. The CH spectrum will be expected to have very few lines. Sweep time in regions with no lines may be decreased by a factor of 10 by sweeping in large steps with only two points per line width instead of 25 to 50, as in conventional analog recording. If a sweep in a given region is unsuccessful, it is important to record the digital data on magnetic tape before going on to a new region of search. Later, if the entire region has been unsuccessfully searched, it is desirable to cover the entire region again using longer averaging times. In an analog recording, the first data is useless and it would be necessary to start a new experiment using a longer time constant. With the computer system the record from all past searches are on magnetic tape and they may be read back into the computer and the new search averaged into the old data. Thus, the results of previous experiments may all be added together to give the equivalent of one long experiment.

With the computer system described, time sharing between experiments is very easy. Our system, however, also carries a very heavy load of small programs, mostly in FORTRAN. During the past three years the system has logged 13,000 hours, about half of which has been computations. This presents many extra problems. The number of users is much larger, many more people need advice and there is always a decision as to whether the student has a programming error or if the system is actually misbehaving. This is a very great liability for any on-line experimentation.

At present, computing has been scheduled at different times than on-line experiments. A new system is just being set up to permit simultaneous programming and on-line use. We plan to time-share the computer between one programmer and many experiments. At present we have edited programs from paper tape, magnetic tape, or typewriter and compiled FORTRAN, but we have not permitted any FORTRAN-compiled program to run while data reduction is underway.

The danger is that a FORTRAN program error might destroy data that has taken a day or more to collect. This danger is also present with the on-line programs but these come from a small group of people, and their programs are very carefully tested and checked before they are permitted to run along with other experiments. In FORTRAN programs one of the biggest problems comes from DO loops and subscripted variables. If the range of the Do loop is calculated in the program, it may work satisfactorily many times. Then with different input data, the range of the Do loop would be calculated to be very large. The program would store data all through the computer, including the data collection programs and buffers.

To prevent this there must be some type of file-protect system. This can be done with an executive or monitor program, but this is far from absolute protection. Furthermore, the monitor system seriously degrades the performance of the computer. The system we have installed is a hardware system and is shown in Fig. 17. It is based on the observation that there is one point which separates on-line experiments from programming. On-line experiments always operate with an external interrupt on. Even when data is being worked up, the second-highest external priority interrupt is on. In programming only the buffer interrupts are used. An exception to this is the lowest-priority interrupt which is asserted from the control panel. This operates a small and simple monitor program which always retains control until the interrupt is released. This is treated as a small data-reduction program even though it operates on the programming system. The status of the external interrupt gives a clean separation of on-line experiments.

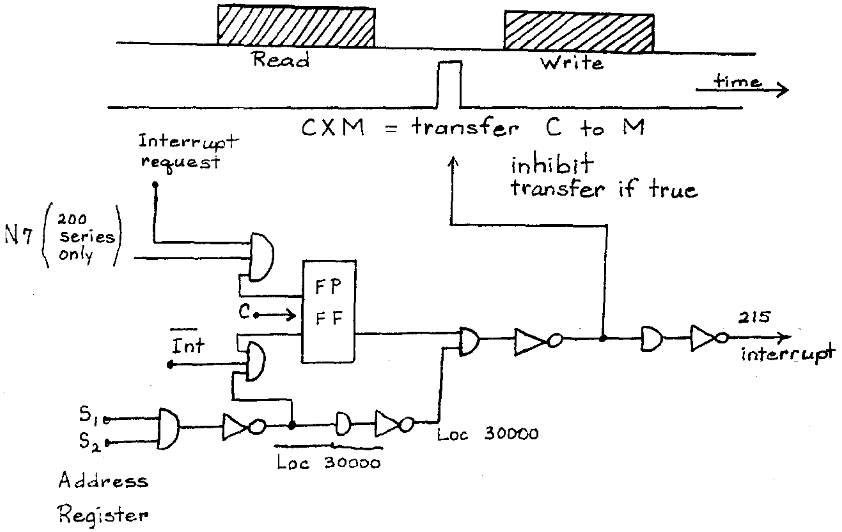

FIG. 17. The memory-file-protect system designed to protect data reduction from computing errors.

In a computer memory, the data in the core is destroyed on reading. It is read into a memory register and later in the cycle it is rewritten in core. If a new word is to be stored, the memory register is changed to the new word before it is rewritten in core. During a computational program the external interrupts would always be off. As shown in Fig. 17, the file-protect flip-flop is normally reset (file-protected). When a computational program attempts to access memory above $30{,}000_8$, the area reserved for data reduction, the changing of the memory register is inhibited. As a result, no data is lost or destroyed. The program might have branched into the 30 thousands. It would then try to execute the number if picked up as an instruction, and this may be something that ties up the computer. To prevent this, the signal to inhibit the changing of the memory register also initiates the third-lowest interrupt. On the next instruction the computer branches to a program which writes a message to the programmer and terminotes the offending program (clears the lower core), and returns control to an idle loop to await the next data-reduction interrupt.

When an external interrupt comes in from a laboratory experiment, the file-protect lip-flop is set to permit use of the upper core. The upper core remains unprotected until the interrupts are all off and control is passed back to the computational program (an address below $30{,}000_8$ is accessed).

In conclusion, we believe computer control is very important in chemical instrumentation, not to automate experiments or to make it easier to do experiments or to relieve the experimenter of the necessity to think, but instead it is important because it permits doing experiments which are otherwise impossible. It permits the measurement of signals which are completely buried in noise and unobtainable in any other known method. It makes possible more accurate experiments. These gains are at the expense of requiring the experimenter to work harder, and to think more about what his data means and how to separate it from stray background signals.

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