Time Resolved Spectroscopy: Stroboscopic and Step Scan Methods

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INTRODUCTION

The characterization of chemical reactions has been an area of intensive research for a number of years. The experimenter may wish to identify the structural changes occurring in the subject molecule as time passes or characterize the reaction kinetics by monitoring the concentrations of the various species involved. The mid-infrared spectrum can provide a great deal of information about these questions. The making and breaking of the various bonds in a molecule can often be readily discerned due to the excellent correlation between observed spectral features and molecular functional groups. By monitoring selected absorbencies in the spectrum, the concentrations of the various species involved in the reaction can be determined by the application of Beer's Law. Regardless of the information being sought, the study of a reaction as a function of time is generally referred to as Time Resolved Spectroscopy (TRS).

The application of the mid-IR to TRS was greatly simplified with the introduction of Fourier transform infrared spectroscopy (FT-IR). The well-known throughput and multiplex advantages of FT-IR make it possible to study a wide range of chemical reactions in a liquid, solid or gas. An FT-IR can routinely collect a spectrum within a few hundredths of a second and therefore reactions that require a time resolution of minutes or seconds are easily characterized.

However, what if an experimenter needs a time resolution that is less than a few hundredths of a second? A variety of techniques are available to achieve this time resolution by FT-IR. The choice of which technique to use depends on whether or not the interferometer can acquire an interferogram and return to the starting position before it is time to acquire the next interferogram. This in turn depends on the resolution required which ultimately dictates the distance the moving mirror must travel. If the resolution required is low (*i.e.*, on the order of 16 cm^{-1} or greater) then the mirror travel is relatively short. The high moving mirror velocities available on the Nicolet System 800 FT-IR make it possible for as many as 50 scans a second to be collected when a resolution of 16 cm^{-1} is adequate for the experiment. If a higher spectral resolution is required or shorter time resolution is needed, then it is necessary to use either a technique called *Rapid Scan Stroboscopic* or *Step Scan* Time Resolved Spectroscopy (TRS).

RAPID SCAN STROBOSCOPIC TRS

Rapid Scan Stroboscopic TRS is a modification of conventional rapid scan interferometry that was developed by A.W. Mantz.[1,2] Rapid Scan Stroboscopic TRS does not acquire an entire spectrum in a single scan; instead a series of time resolved interferograms are simultaneously collected, a small piece at a time, through the use of an ingenious data sorting scheme. This can be illustrated by considering the following hypothetical experiment.

Assume that a gaseous cyclic molecule **A** becomes a linear species with several double bonds when placed in an excited electronic state. The molecule can easily be excited by exposing it to a brief flash of intense radiation from a xenon flashlamp. The ring will open and form double bonds after 40 microseconds (μs) have elapsed. Assume also that the reaction is reversible and that **A** will reclose 280 μs after excitation. This type of experiment is commonly referred to as an *impulse-response* experiment since it is the response (the ring opening and reclosing) to an impulse (the flash of intense radiation) that is being measured. Finally, assume that it is the structural changes that are of interest.

To measure this reaction, a gas cell with IR transparent windows and a xenon flashlamp is designed; the design of this hypothetical cell is shown in Figure 1. To assure that no *inter*molecular reactions occur, a low gas pressure of **A** is used. Because the reaction is gaseous and at a low pressure the natural bandwidths of the IR peaks will be narrow and therefore desirable to measure the spectrum at a high resolution. However, because structural information is desired, the spectra is recorded at a resolution of 1 cm^{-1}; this requires an interferogram that has 16,384 data points starting from the zero-path difference point. Finally, it is desired to take the interferogram at 20 μs intervals beginning 20 μs after the excitation pulse. Because the reaction is complete within 280 μs after the excitation pulse, a total of 14 interferograms will be acquired.

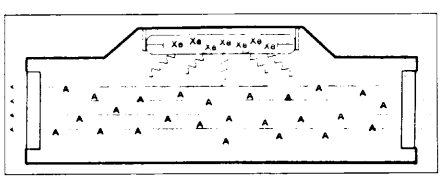

Figure 1 *Reaction cell with xenon flashlamp.*

One of the requirements of rapid scan stroboscopic TRS is that the start of the experiment must be controlled by the FT-IR instrument. In this hypothetical experiment this means that the flashlamp is controlled by the FT-IR computer. The reason for this is that the spectrometer uses the reference laser zero-crossings to clock the taking of the data. The velocity of the moving mirror is set such that a full laser fringe (two reference laser zero-crossings) is transversed at 20 μs intervals. This requires a moving mirror velocity of 1.58 cm/sec. (316 nm per fringe divided by 20 μs). The timing of the start of the experiment becomes extremely critical and therefore must be controlled by the interferometer computer. In addition, the interferometer computer must know the position of the moving mirror relative to the zero-path difference point. The computer does this by counting the number of reference laser fringes the moving mirror has traveled past the zero-path difference point and by noting the direction of travel.

When the gas cell and interferometer are ready the experiment begins. The interferometer is brought to the starting point and the scan begins. The interferometer computer triggers the flashlamp one full laser fringe before the first interferogram point is reached; this is made possible by the fringe counting system on the interferometer computer. By the time the moving mirror travels one full laser fringe past the point where the flashlamp has fired, 20 μs have elapsed. The signal taken from the detector at this time becomes the first point of the 20 μs interferogram. When the mirror has traveled a distance equivalent to two laser fringes then 40 μs have elapsed since

the flashlamp was fired. The signal from the detector becomes the first point of the 40 μs interferogram. The signal taken from the detector when the third laser fringe has passed becomes the first point of the 60 μs interferogram. The detector signal at the fourth point becomes the first point of the 80 μs interferogram and so forth. Process continues until the first data points for all 14 time resolved interferograms have been acquired. This entire process is illustrated in Figure 2.

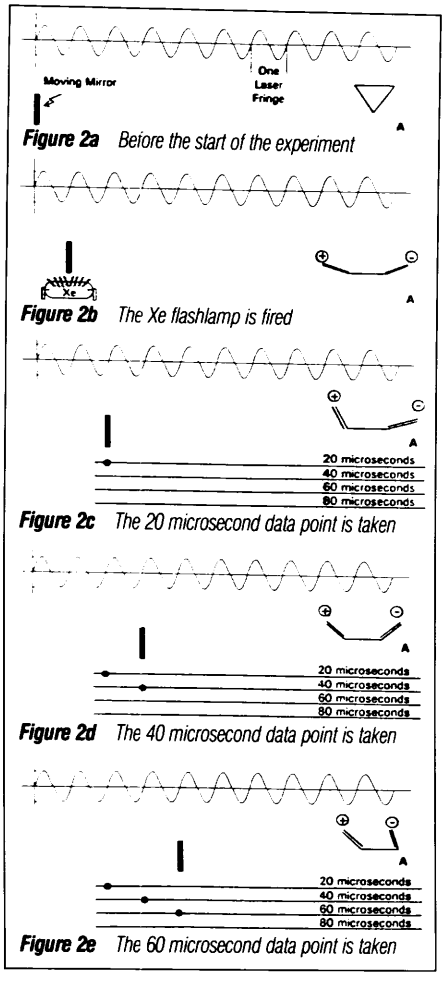

Figure 2a *Before the start of the experiment*

Figure 2b *The Xe flashlamp is fired*

Figure 2c *The 20 microsecond data point is taken*

Figure 2d *The 40 microsecond data point is taken*

Figure 2e *The 60 microsecond data point is taken*

After 280 μs have elapsed, **A** has completely returned to its original cyclic state. After the interferometer returns to its starting position the experiment is repeated so that the second data point of the time resolved interferograms may be collected. However, the flashlamp is not triggered at the same reference laser fringe as the previous scan, but rather the firing is delayed until the mirror has moved one full laser fringe from the previous location (in other words, where the first data point was taken from the 20 μs time resolution interferogram). If the flashlamp was set off at the same laser fringe as the previous time, the moving mirror will have reached the second data point of the 20 μs interferogram after 40 μs have elapsed. The 20 μs data is gone, and no new time resolved data is available. This sequence involves the delaying of the flashlamp triggering point one laser fringe, taking the data points, waiting until **A** has returned to its original form, and then beginning again until all 14 time resolved interferograms are constructed.

It is useful to examine the above process in more detail to illustrate the features and drawbacks of rapid scan stroboscopic TRS. First, the question may be asked why all 14 time resolved interferograms are being taken simultaneously. It is possible, for instance, to simply trigger the flashlamp, wait until the moving mirror has transversed one laser fringe, take the data point, and then simply repeat the process until all of the necessary data points for the 20 μs interferogram have been acquired. This sequence can be repeated for the 40 μs interferogram except that the data points are taken after two reference laser fringes have been transversed after the flashlamp was fired. However, this is extremely inefficient. Consider that to complete a 1 cm^{-1} resolution interferogram the experiment must be repeated 16,384 times. Therefore, to fill all 14 time resolved interferograms the experiment would have to be repeated *229,736 times.* This is unacceptable.

The data collection is made more efficient when data for all 14 interferograms are taken after a single firing of the flashlamp. This also lowers the experimental measurement time which is necessary to reduce the effects of instrument and experiment variability (for example, the power generated by the flashlamp may change after a large number of firings). It is also possible to further reduce the total time required to complete the time resolved interferograms by repeating the experiment several times during the course of a single scan. In our hypothetical experiment, the reaction is complete after 280 μs have elapsed. To be absolutely sure the reaction is complete, the waiting period is increased by a factor of 10 to 2,800 μs. However, the interferogram requires 327, 680 μs to complete a single scan. It is possible to repeat the experiment over 100 times during the course of a single scan, assuming that the flashlamp can be cycled quickly enough. The time required to collect 14 interferograms that are composed of a single scan becomes less than 10 minutes (Figure 3 illustrates this process).

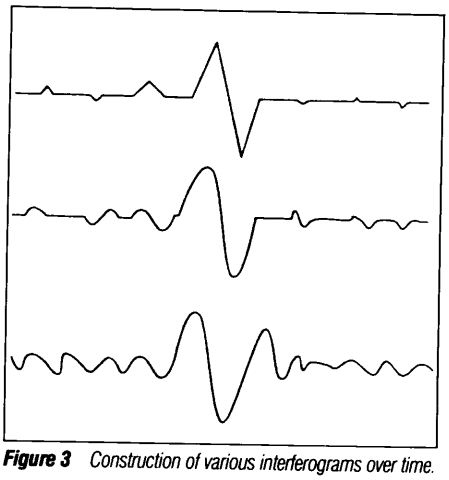

Figure 3 *Construction of various interferograms over time.*

It is also apparent from the above that rapid scan stroboscopic TRS *can only be applied to experiments that are extremely reproducible.* **This requirement applies to any experiment where it is not possible to acquire the necessary spectral information as a series of sequential complete scans.** In the hypothetical experiment the **A** returns to its original state after a brief amount of time. Since the molecules of **A** are contained within a sealed cell, the concentration will remain constant throughout the entire experiment; moreover, experimental conditions like cell alignment will remain constant because the cell does not need to be manipulated once the experiment has begun. Thus meeting the requirement for experimental reproducibility becomes very simple. On the other hand, consider what would happen if the reaction lead to the formation of a stable product (for instance, the gas pressure was increased to a point where **A** started to irreversibly dimerize when placed in an excited state. If this were to occur, then every time the flashlamp was fired the cell would have to be flushed and a fresh batch of reactants added. It would be extremely difficult to precisely duplicate the reactant concentrations each time the experiment was run; in addition, there are practical constraints of time as well as cost and availability of the reactants involved.

Another feature is that the time between detector readings is governed by the velocity of the moving mirror. The range of available time resolutions depends on the range of moving mirror velocities available. Small errors in the moving mirror velocity will be reflected as a variance in the interval between taking detector readings.

In summary, what can be concluded about rapid scan stroboscopic TRS? The method is exceptionally good for repeatable

experiments where the time resolution is between 10 μs and the time required for the interferometer moving mirror to complete a scan and return to the starting position. This will depend on the resolution as well as the velocity. The method makes full use of the multiplex and throughput advantages of FT-IR. Rapid scan stroboscopic TRS also makes full use of the multiplex and throughput advantages of FT-IR. The method requires no special equipment other than a means of connecting the interferometer controller to the experiment initiator. However, this is also one of the disadvantages of the technique since it restricts the application of rapid scan stroboscopic TRS to impulse-response experiments.

There are experiments where the use of rapid scan interferometry is undesirable. For instance, if it is necessary to use phase sensitive detection (a lock-in amplifier) then the use of rapid scan interferometry is impractical because there is no single frequency available to use as a reference. This is due to the interferometer modulating each wavelength of light emanating from the source at its own frequency. In these experiments, step scan time resolved spectroscopy is the technique of choice.

STEP SCAN TIME RESOLVED SPECTROSCOPY

The technique of step scan TRS was first described by Sakai and Murphy[3] and more recently by Palmer *et al.*[4] In step scan interferometry, the moving mirror is stopped and held at equally spaced points, thereby stopping the modulation of the source radiation. However, most IR detectors require that the radiation be modulated. Therefore it is necessary to modulate the radiation with a slotted wheel (generally referred to as a mechanical chopper), by placing a dither on one of the mirrors (referred to as phase modulation) or by changing some property of the sample itself with a perturbation that is applied at a constant frequency. These modulation methods vary all the wavelengths of light emanating from the source at the same frequency. Therefore, a reference frequency is available that makes the use of devices such as lock-in amplifiers feasible.

In order to achieve a time resolution on the order of microseconds, it becomes necessary to modulate the radiation at an extremely high rate. Devices like choppers act much like a movie camera. For instance, assume that a movie is being made of a ball being dropped. If the rate at which the film is passing the lens is slow enough, then the ball will appear as a blur on each frame. This is because the film integrates the image of the ball falling during the time it is in front of the camera lens. By speeding up the rate at which the film passes the lens, the image of the falling ball on each frame becomes less and less blurred. When the film is moving fast enough, the image of the ball becomes resolved to an image of the ball itself; the ball moves a small amount on each frame.

When a mechanical chopper is used the detector is exposed to light 50% of the time. For instance, if the chopper is modulating the light at 100 Hertz (Hz) then a complete on/off cycle, or period occurs every 1/100th of a second; moreover this means that the chopper is open for 5 milliseconds and then closed for an equal amount of time. During the time the chopper is open, the detector is averaging the light that is irradiating it. Therefore, it is not possible to look at an event that is of shorter duration than the time the chopper is admitting light to the detector.

In addition to the problem of modulating the light at a very high speed, there is also the problem of demodulating the detector signal before the value is included in the interferogram at a particular retardation. The signal from the detector at a given retardation is composed of a sinusoid; the interferogram on the other hand, is composed of a series of dc values that were each recorded at a particular value. This varying signal is converted to a dc signal by means of a lock-in amplifier or similar phase-sensitive detector. Lock-in amplifiers require a finite amount of time to demodulate the signal (generally 5 to 10 cycles) and therefore it may not be possible to detect an event that is much faster than the modulation rate.

In either case, it is possible to circumvent these problems by using a detector that does not require a varying signal. These detectors are called dc coupled detectors. When a dc detector is used, the fastest event that can be recorded will be dependent solely on the detector rise time, which is a measure of how fast the detector will respond to a change in the signal level, or on how fast the supporting electronics (the analog-to-digital converter or recorder) can operate. A disadvantage of dc coupled detectors is that the small change in signal which is due to the event being studied may be obscured by a large constant level which may be included as part of the detector signal.

Assuming that a satisfactory method of detecting the signal is found, then time resolved spectroscopy using step scan interferometry becomes very simple. Once the mirror is stopped, an external clock is used to determine when the signal is taken from the detector. Thus if the experiment on **A** was studied using step scan interferometry, then the sequence of events would be for the mirror to move to a retardation point and stop; the flashlamp is then fired and a clock is used to determine when the signals are taken (this is illustrated in Figure 4).

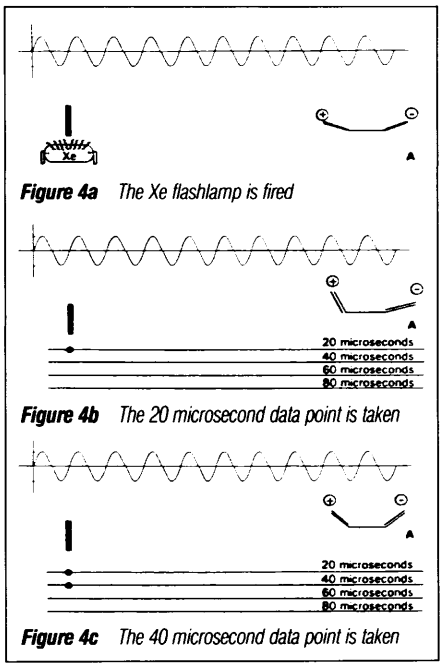

Figure 4a *The Xe flashlamp is fired*

Figure 4b *The 20 microsecond data point is taken*

Figure 4c *The 40 microsecond data point is taken*

Step scan TRS has some advantages when compared to rapid scan stroboscopic TRS. First, because the taking of the detector signal is timed by an external clock, then it is possible to take signals at irregular intervals (for example, a signal may be taken at 1, 2, 5, 9, 11 and 20 microseconds). In addition, the various time resolved interferograms are filled in a linear fashion as opposed to using a complicated data sorting scheme. This may make the experimental set-up easier to comprehend. Finally, the experiment no longer has to be controlled by the interferometer computer; instead, once the mirror has stopped, the experiment may be triggered at any time. The primary disadvantage of step scan TRS is that some IR detectors require the source radiation be modulated, which in the case of step scan interferometry means that an external means of modulating the radiation will have to be incorporated into the experiment. This is an intrinsic part of the rapid scan stroboscopic TRS method.

Step scan TRS, however, has the same restriction as rapid scan stroboscopic TRS—the experiment must be repeated for each point in the interferogram and therefore the experiment must be highly reproducible.

Is one method better than the other? The answer is no. Each method has its advantages and disadvantages when compared to each other and both require the experiment be repeated for each point in the interferogram. Overall, each have their place in the laboratory.

REFERENCES

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4. Palmer, R. *et al.* (1989) *Appl. Spectrosc.*, **43**, pg. 193.

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