Time Resolved Infrared Spectroscopy using both Step-Scan and Rapid-Scan Methods


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Time resolved FTIR is a spectroscopic technique whereby transient processes in the range of a couple of seconds to those in the low nanosecond range can be measured. Time resolution in the UV-Vis region was accomplished before that of FTIR\(^1\). This is mainly because UV-Vis spectroscopic measurements are not detector noise limited as are IR measurements. This is mainly due to a large noise equivalent power (NEP) of IR detectors\(^2\). A particular wavelength can be monitored with relative ease in the UV-Vis but in the IR, a dispersive instrument will not have the throughput to make this measurement without great difficulty. UV-Vis time resolved techniques however, suffer immensely from molecular absorption band overlap. This is not a problem in studying molecules in the IR for three main reasons\(^1\): 1.) Each molecule possesses a characteristic fingerprint in the so-called fingerprint region. This largely eliminates interference due to the solvent or other species present. 2.) All molecules that vibrate can be viewed somewhere in the IR region. 3.) Transient species can be identified from parent species by a specific change in vibrational properties. With these advantages of IR spectroscopy came the desire for time resolved measurements using FTIR.

As mentioned, the noise equivalent power (NEP) of IR detectors are much higher than in the UV-Vis. This problem is largely overcome with the use of a Michelson interferometer in an FTIR as will be shown. A Michelson interferometer uses a moving mirror, stationary mirror, a beam splitter, and a reference HeNe laser to monitor mirror movement. Light comes into the
interferometer and is split about 50% at the beam splitter. Half the light goes through the beam splitter to the stationary mirror and the other half is reflected up to the moving mirror. As the light is recombined after reflection it is modulated at a new frequency \( f \) where \( f = 2V/\ddot{e} \) and \( V \) is the velocity of the moving mirror. The velocity of the moving mirror is known precisely by the oscillating cosine wave created by the HeNe laser. As will be seen, a constant velocity is critical to collection of interferograms in order prevent a degradation of the S/N. A basic diagram of a Michelson interferometer is shown below³.

As seen above, each wavelength of light will be modulated at a new frequency based upon a constant velocity. Light will then be combined constructively and destructively based on the length of travel of reflected light off the moving mirror. Light is totally constructive at integers multiples of \( \ddot{e} \) and totally destructive at half integers of \( \ddot{e} \). In between there is a combination of the two. At \( \ddot{e} = 0 \), all the light goes through at full intensity and creates the center
burst. Intensity is a function of $\bar{a}$ and as you move the mirror your intensity changes due to interference. Once you move the mirror the entire pre-defined distance, a series of points will be collected with a particular intensity corresponding to its particular $\bar{a}$. The result is an interferogram based on the modulation of light entering the interferometer. This data will then be transformed from the $I$ vs. $\bar{a}$ domain into the frequency domain via a fast Fourier Transform.

The FTIR based on the Michelson interferometer offers three distinct advantages: the multiplex advantage, Jaquintos or throughput advantage, and resolution being determined only as a function of mirror displacement $\bar{a}^4$. The first mentioned allows all resolution elements to be measured simultaneously since all the light will reach the detector at the same time. The end result is a rapid acquisition of an entire spectra. The second advantage is of utmost importance for the use of FTIR for time resolved spectroscopy. As mentioned above, IR was in the past limited in its use for time resolved studies because of the large NEP of IR detectors. If you allow all your light to reach the detector you are increasing the overall throughput and your signal is maximized. This is crucial since you will often be measuring only small changes in signal throughout a transient process. The third advantage allows for tremendous spectral resolution since resolution is only dependent on the total mirror displacement by the relation $\bar{A}\bar{a}=1/\bar{a}$. Therefore if you want to increase resolution you only need
Since a Fourier Transform of the acquired interferogram is a complex transformation process, FTIR was limited in its use until technology was available to handle the extensive data produced. Once technology allowed for the practical use of this powerful technique, time resolved studies in the IR region began. There are two main time resolved FTIR instrumental designs, rapid-scan FTIR time resolved spectroscopy (FTIRTRS) and step-scan FTIRTRS. These two techniques are significantly different but achieve the same ultimate goal, which is the temporal and spectral resolution of a transient process. The first to be discussed is the rapid-scan technique.

Rapid-scan FTIRTRS can be divided into two categories as well. The different rapid-scan techniques are based upon a rapid succession of events in one mirror scan or a single event per mirror scan. Both methods of rapid-scan FTIRTRS are based on the principle of collecting data while the mirror scans.

Rapid-scan studies were first done creating a transient event via an external light source such as a flash lamp\textsuperscript{6,7}. This method of photolysis creates a change in the molecule that can be measured by either the emission or absorption of IR radiation. This transient state can then be explored temporally by defining a time resolution element of interest. The only caveat is that if you wish to acquire a spectra with one mirror sweep the transient event must last longer than the scan period. If the transient event is shorter than a single mirror sweep a series of external perturbations (i.e. laser pulse or flash lamp pulse) may be applied to the system and data collected between each perturbation\textsuperscript{8}. 
For the case of multiple events per mirror sweep, many considerations must be made. It is absolutely critical to have a proper timing sequence between your external event, FTIR, and data acquisition. It must be noted that you are collecting a series of temporally and spatially resolved spectra. If the mirror movement is out of phase with the triggered event even the slightest bit you will experience increased noise which is especially a problem with small spectral changes\(^9\). This is because spatial and temporal resolution are directly linked. If you collect a data point(s) corresponding to a particular time element at the incorrect \(\hat{t}\), when you combine your data points and transform you will see the phase variations directly in the spectra as noise.

Another consideration that must be made is that if you define a particular time element(s) to sample between each event, the event must be over before the next perturbation and series of sampling points begins\(^9\). As an example, if you apply an external perturbation every \(n\) 200\(\mu\)s with a 10\(\mu\)s pulse width, data collection every 20\(\mu\)s from 30 to 190\(\mu\)s, the resulting transient must be over before the next pulse at 2\(n\) 200\(\mu\)s. This may require undersampling. The amount of undersampling will be determined from the Nyquist theorem that says that you must sample at 2x your highest modulated frequency. This is directly determined in part by mirror velocity, which leads into another major consideration.

As was seen in the equation above, \(f=2V/\hat{\epsilon}\). Therefore your frequency bandwidth is determined in part by the velocity of the moving mirror. If you
increase velocity you increase your frequency bandwidth provided you keep \( \Delta \phi \) the same. As is known, white noise will increase by the \( \Delta f \). This means that \( S/N \propto 1/\Delta f \) and \( S/N \) will decrease as you increase \( \Delta f \).

With these general considerations in mind you can then determine the type of time resolution that is possible and/or desired. The basic principle behind multiple transient events per mirror scan is that you will acquire a series of data points corresponding to a particular \( \Delta \) which also is your time element chosen. The total event time is divided up into the perturbation event and time element(s). You will apply a laser pulse to your sample for example and data will be taken after a short period of time. If more than one time element \( t_i \) is to be sampled per event, after another short time period another data point will be taken corresponding to \( \Delta t_i \). The pulse is then repeated after the collection of the desired number of data points from the first pulse has completed. This repeat pulse occurs at another retardation value as well as the time elements that follow. Usually the time between data collection is at equal time intervals \( \Delta t \).

The data collection and sample event are usually controlled by the interference pattern of the HeNe laser fringe. The process is repeated until a complete scan occurs. The scan can be repeated if desired to collect more data or for signal averaging. If multiple scans will be taken to compile data points, you can delay the onset of the first sample event so that each \( t_i \) and perturbation event will occur at some \( n \Delta t \). This is illustrated below:
These data points corresponding to the time elements $\Delta t$ will then be stored until enough data has been collected. Upon completion of data collection, the individual time elements will be combined and their respective interferogram assembled. The result is a series of interferograms corresponding to a particular time $t_i$. It should be noted that it is essential that the sample event be highly reproducible. The end result after transforming your data is a temporally and spatially resolved set of spectra. An example of this type of method can be seen below.
As was mentioned above, usually the HeNe laser fringe pattern controls an external delay generator or an equivalent device for time delay of the event perturbation, mirror movement, A/D conversion, and data acquisition. A general description is shown below:\textsuperscript{10}:

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![Diagram of timing sequence](image)

**Figure 2.** Time-resolved FTIR emission spectra collected by using the arrangement shown in Figure 1, with a CO\textsubscript{2} laser modulation frequency of 1.57 kHz. The interferograms were collected by using 32K data points (0.5-cm\textsuperscript{-1} resolution) and one laser shot per data point. Note that the laser was operating simultaneously on three laser lines (P\textsubscript{s1} 949.3 cm\textsuperscript{-1}, P\textsubscript{s2} 945 cm\textsuperscript{-1}; and P\textsubscript{32} 942.4 cm\textsuperscript{-1}). The IR source of the interferometer was left switched on during the data collection to aid the subsequent phase correction of the interferograms. The time delay between each FTIR-TRS trace is \( \sim 15 \mu s \). The whole set of spectra spans 280 \( \mu s \).
As was mentioned above, if the transient event is sufficiently long a single mirror scan corresponding to a single time element $t_i$ can be done as well. This implies that once your transient process has occurred and a desired $t_i$ is selected, you wait a time period $\Delta t$ and begin your scan. The entire scan must occur however within the desired time element. Another requirement is that the entire sampling process (sample event and data acquisition) occur before the start of then next scan$^{11,12}$. This ensures in phase processing. The event can be repeated multiple times to signal average. It must be mentioned that if you wish to explore other time elements, a separate series of scans corresponding to the new $t_i$ must be performed with a delay of $n\Delta t$.$^{11,12}$ Measurement of a single scan temporally resolved transient process by rapid-scan FTIRTRS is only limited by the scan rate of the mirror, detector rise time, and digitization.

The other approach to FTIRTRS is that of step-scan. In step-scan FTIRTRS the dependence of constant mirror movement on data acquisition is removed$^8,2$. Step-scan FTIRTRS is restricted to only a highly repeatable process whereas rapid-scan can monitor a dynamic process that occurs only one time for reasons mentioned above. In Step-scan FTIRTRS you create an external event by one of the methods already mentioned and then collect data at a particular stationary mirror position. A time element is chosen and data is acquired after $\Delta t$. The mirror then moves to the next specified position that is dictated by the spectral resolution chosen and stops. The sample event is repeated and data is obtained. The entire process repeats until the scan is complete. As in rapid-
scan FTIRTRS the transient between two sample points must end before triggering the next event.

You may sit at a particular à and collect multiple data points to eventually signal average. If the same particular tᵢ is to be collected at a particular à the sample event must be repeated for each data point however⁸. Another option is to collect different time elements at each mirror position. These data points will correspond to a particular à and also a particular time element. Once all data is collected, the points will be sorted based on retardation and time. Upon completion, the corresponding interferograms will be assembled. Essentially, only detector rise time and digitization limit temporal resolution². Incredible spectral resolution is able to be accomplished because you can increase the mirror path-length as much as is desired. This is due to the fact that you are stepping the mirror in certain increments, not scanning continuously. This means that the transient lifetime is independent of the total mirror displacement. This differs from rapid-scan because if you wish to acquire a complete scan before the end of a transient process you are limited by mirror displacement. Johnson et al. report low nanosecond time resolution using step-scan methods with excellent spatial resolution as well.

Mirror position is also essential to step-scan measurements and is accomplished again by monitoring the HeNe laser fringe pattern. Smith et. al.¹³ describe a method for monitoring the position of the mirror. When the mirror stops a settling time occurs and it is oscillated rapidly. This causes a change in
the HeNe laser fringe at a particular $\alpha$ which is defined by the spectral resolution chosen. This predefined change in the HeNe laser fringe, according to mirror oscillation, will tell the computer whether or not the mirror is in the correct position.

To better understand this principle, assume the mirror advances at every $\alpha/4$. Since the laser fringe will oscillate from positive to negative values, a periodic oscillation of the mirror will cause two different changes in the interference pattern. At every zero crossing one of the patterns will exist and at the maxima the other change in interference fringe will be observed. If the mirror is out of position these particular oscillatory changes will not be observed. The computer will sense this and the mirror will be repositioned.

Time resolved FTIR by either of the two methods mentioned are powerful techniques for measuring short-lived processes. The perturbations mentioned are by far not the only way to initiate a transient process. Deformation studies of polymers using a mechanical stretcher$^{11,12}$ and stopped-flow mixing of chemicals for use with rapid scan$^{14}$ are a couple of examples of other transient initiators. The events that can be studied are also seemingly limitless. A couple of popular systems studied have given much attention to time resolved FTIR and are those involving photoexcitation of bacteriorhodopsin$^{15,16,17}$ and those involving transition metal complexes$^{18,19,20}$. Both techniques have their advantages and disadvantages. The major downfall of rapid-scan is the limit in time resolution for reasons mentioned. Rapid-scan also suffers more S/N
problems for reasons such as out of phase sampling, white noise, and spectral artifacts. Rapid-scan does however hold one distinct advantage over step-scan and that is its ability to resolve single dynamic events. Step-scan suffers one major downfall and that is that data acquisition is longer than rapid-scan. The benefits of step-scan FTIRTRS are substantial however. As was shown, low nanosecond time resolution is possible along with a better S/N ratio than rapid-scan. Step-scan also separates temporal and spectral resolution by acquiring data at stationary mirror positions. The choice of technique is totally dependent on the application at hand.

Sources Cited