

# Step-scan Time Resolved Spectroscopy on the Nicolet Magna-IR® 860 Research Spectrometer

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## KEYWORDS

*FT-IR, step scan, time resolved spectroscopy, kinetics, rapid scan, cyclic electrochemical reaction, liquid crystal*

## INTRODUCTION

The Magna-IR 860 E.S.P. spectrometer combines high performance and advanced data collection technology with unlimited research capabilities. Nicolet Instrument Corporation has added to these advanced capabilities by producing a complete fast time resolved spectroscopy (TRS) package for the Magna-IR 860 research spectrometer. The technique of step-scan time-resolved spectroscopy is used to record spectra of transient species whose change of interest occurs faster than the time resolution available in rapid-scan (linear-scan) modes.

For a rapid scanning instrument the fastest continuous resolution available is 45-50 Hz. The limit of direct rapid-scanning observation is an event of duration of about 250 milliseconds, using the rule of thumb that approximately five points are required to characterize the shape of the event satisfactorily. The principal requirement for a fast time resolve experiment is that the chemical system being analyzed must be repeatable and reproducible. Examples of some time resolve experiments include: cyclic electrochemical reactions, light induced chemical reactions (photocyclic reactions), gas-phase photodissociation/association reactions, and laser emission experiments.

Step scan TRS data collection is achieved in the Nicolet Magna-IR 860 spectrometer by precise control of the interferometer moving mirror. Instead of scanning the moving mirror with continuous motion as in a typical FT-IR experiment, the moving mirror is stopped at discreet data collection points (typically every other HeNe laser crossing). At each data collection or optical retardation point, the time resolved event is triggered. Then, a series of data points are collected and sorted based on

time relative to the event trigger. The moving mirror is then stepped to the next optical retardation point, and the process is repeated. In this manner, step-by-step, a complete series of time separated interferograms is collected. Figure 1 illustrates a set of time-slice interferograms collected with step-scan spectroscopy.

Precision control of the moving mirror during the step scan measurement is critical to the success of the experiment. Any motion or vibration of the mirror during the data collection will result in inherent noise in the Fourier transformed spectroscopic result. The Nicolet Magna-IR 860 spectrometer employs a superior servo control system that is based on the application of a digital signal processor (DSP) to directly control the moving mirror. Using the DSP, the interferometer motion is maintained using an adaptive, closed loop, proportional-integral servo control algorithm. The position is maintained by DSP monitoring of the laser fringe information from a DC coupled laser detector in the interferometer. One advantage of the Nicolet implementation of step scan is that the DSP can hold the mirror at each step for tens of seconds (essentially infinitely), and can reproducibly reposition the mirror with a positional accuracy of better than 0.2 nanometers. Another advantage of the Nicolet implementation is that it is nearly immune from vibration induced (environment) noise. Furthermore, dynamic alignment of the interferometer is maintained in between successive steps. Thus, the DSP control and dynamic alignment of the interferometer provides excellent positional accuracy and long term stability for step-scan experiments.

In addition to the basic step scan capabilities of the Magna-IR 860, the TRS package consists of three parts: 1) a high

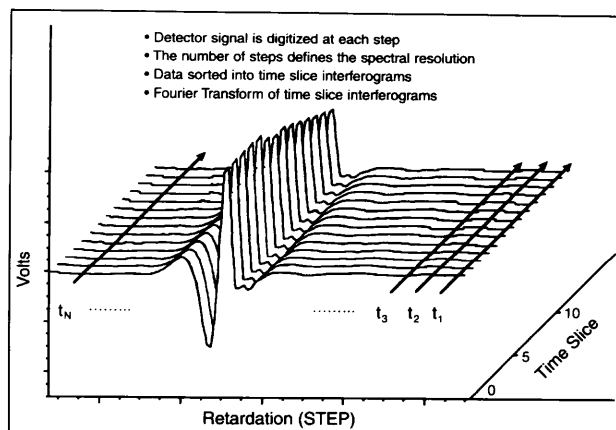


Figure 1: An illustration of the data acquisition of step-scan time-resolve interferograms

speed analog-to-digital (A/D) converter, 2) an AC and DC-coupled photoconductive or photovoltaic detector (either MCT or InSb) and matched high-speed pre-amplifier and 3) a TRS add-on module to the Research OMNIC® software. Several analog-to-digital converter options are available for the Magna-IR 860 TRS package, including a 5 MHz 12-bit A/D converter, a 100 MHz 8-bit A/D converter or a 100 MHz 12-bit A/D converter. Automatic gain ranging of the interferogram signal is employed so the most significant A/D bits are always sampled. The 5 MHz digitizer provides 200 nanosecond time resolution. The 100 MHz digitizer has a sampling rate of 10 nanoseconds but the ultimate time performance is dependent upon the detector and pre-amplifier response times.

The standard photoconductive MCT detector is capable of performing step scan TRS measurements to about 100 microseconds time resolution. The standard photovoltaic MCT detector can achieve time resolutions of better than 100 nanoseconds. Custom detector/pre-amplifier combinations may also be purchased for even faster time resolutions.

Research OMNIC E.S.P. with TRS Data Collect software provides the researcher the ability to perform complete collection and spectral processing of the temporal information. The TRS software provides the researcher with the temporal data in any desired format: interferograms, single

beam (unratioed spectra), or ratioed (*i.e.* transmission/absorption) spectra. Consistent use of OMNIC is followed for the TRS experiment so no unpacking or resorting of the data is required by the user.

The Nicolet Magna-IR 860 TRS Data Collect software package provides a number of software controlled parameters for the monitoring of temporal events. Interferogram data collection parameters include: spectral resolution, points before peak (adjustment for single sided data collection) and sample spacing (under- and over-sampling of the interferogram at multiples of the HeNe laser frequency). Temporal data collection parameters include: adjustable settle time for step-scan operation, pre-/post- trigger interval adjustments, number of time samples, sample (temporal) spacing between adjacent time slices, and total number of co-added scans for signal averaging.

One unique data collection scheme in the Nicolet TRS system is the software option to perform logarithmic temporal sampling. Instead of having a constant linear sampling rate, a data reduction scheme is used to provide logarithmic sampling of the event. This provides the advantage of sampling the initial portion of a time resolved event at a high sampling rate, followed by an increasing time separation as the experiment progresses. This is especially useful for exponential decay measurements. Regardless of whether a linear or logarithmic sample spacing is selected, the user is provided a software screen that illustrates the triggering and sampling times that are defined for the experiment. The number of samples (time interferograms) that can be collected in a

measurement is dependent upon the sampling rate and the available memory on the transient digitizer. However, the minimum configuration allows for the capture of at least 100 time slices.

During the data collection, Research OMNIC with TRS Data Collect software provides a live display of each interferogram (time slice) so the researcher can monitor the progress of the experiment (Figure 2). In addition to each individual time resolved interferogram, a static interferogram is also collected using the standard Magna-IR 860 internal analog-to-digital converter. This interferogram is useful where it may be interesting to determine differential absorption measurements between the dynamic time resolved spectra and the static steady state spectrum.

To demonstrate the capabilities of the Nicolet step-scan time resolve spectroscopy package, a model cyclic electrochemical experiment was performed. The remainder of this application note details step-scan time resolve measurements of liquid crystal reorientation dynamics. Electrochemical liquid crystal dynamics provide a repeatable and reproducible event in a time regime that is ideally suited for step-scan time resolve spectroscopy<sup>1,3</sup>.

## EXPERIMENTAL

The sample used in this experiment was a nematic liquid crystal, 4-pentyl-4'-cyanobiphenyl (5CB). A transmission cell was prepared by using two germanium (Ge) windows with a 10 micrometer Teflon spacer into which a liquid crystal system (5CB) was introduced. Germanium is a

convenient window material for transmission of mid-infrared radiation and its conductivity provides utility as an electrode material for the electrical excitation of the liquid crystal molecules.

The interior Ge surfaces of the cell were treated which produced a preferential alignment of the long axis of the liquid crystal molecules (nematic director). The interior surface of the cell was wetted with a 0.1% solution of polyvinylalcohol, the film was allowed to slightly dry, then the film was rubbed in a uniaxial direction with a cotton swab. When dry, the PVA provides microgrooves into which the liquid crystal lies oriented along the direction of the grooves. The cell is assembled with the treated window surfaces placed face-to-face in an antiparallel orientation to the rubbing direction. The 5CB was introduced into the cell via capillary action. Copper tape ring electrodes were placed on the outside faces of the cell and were connected to a pulse generator.

Figure 3 illustrates the liquid cell assembly. An initial infrared static polarization measurement (parallel ( $A_{||}$ ) and perpendicular ( $A_{\perp}$ ) polarization to the nematic director) was performed to verify that the liquid crystal material was aligned properly in the liquid cell. This measurement involved measuring a sample (sample and polarizer) and a background spectrum (polarizer only) for the parallel and perpendicular polarizer orientations, with subsequent processing to produce and absorbance spectrum.

A trigger signal from the Magna-IR 860 spectrometer was used to initiate a square wave voltage pulse across the cell. The

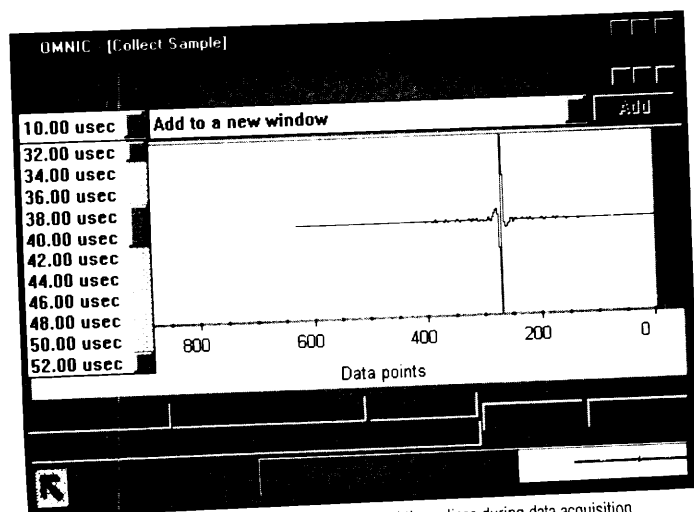


Figure 2: Real time display of scan time-resolve spectral time-slices during data acquisition

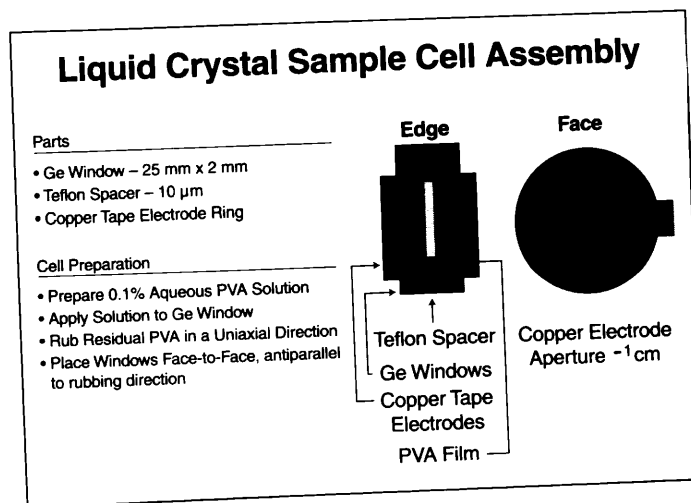


Figure 3: Liquid cell assembly

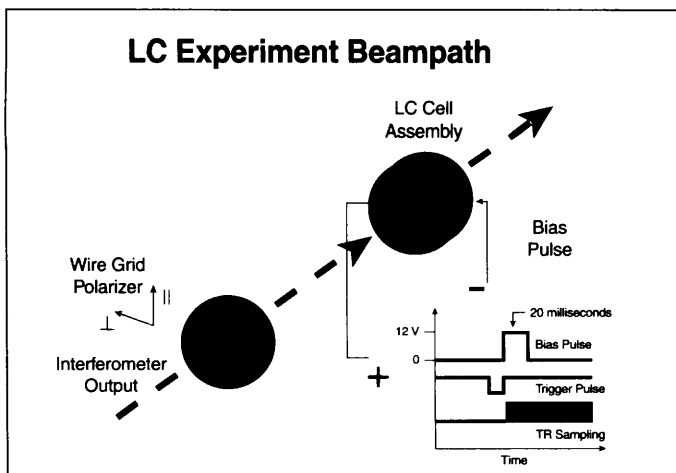


Figure 4: Sample compartment arrangement

pulse had a voltage of 12 volts and a duration of 20 milliseconds. The cell voltage pulse was delayed for 20 milliseconds after the main trigger event. A wire grid polarizer and the liquid cell was placed in the instrument's main sample compartment.

Figure 4 illustrates the sample compartment arrangement. Time resolve spectra were collected with both linear and 1.1 logarithmic time base sampling, with the initial sampling interval being 1000 microseconds. The total time of the measurement data collection was approximately 1 hour.

Figure 5 illustrates an example OMNIC step-scan time-resolve step-scan set-up

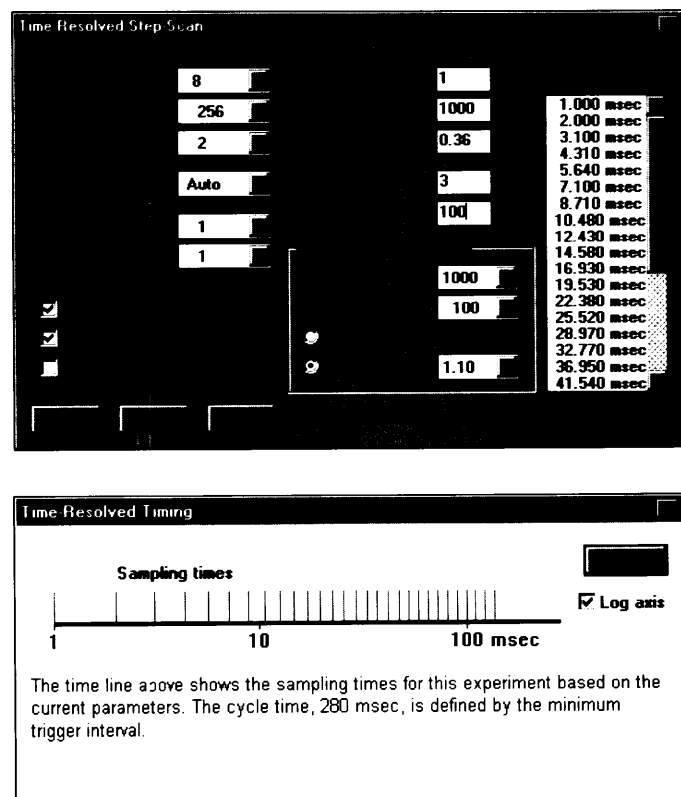


Figure 5: OMNIC Step-scan Time-resolved Spectroscopy set-up screen and experiment timing diagram

| Liquid Crystal<br>Vibrational Band Assignments                                       |                                 |
|--|---------------------------------|
| <chem>NC-c1ccc(cc1)-c2ccc(cc2)C5H11</chem><br><b>4-pentyl-4'-cyanobiphenyl (5CB)</b> |                                 |
| Wavenumber (cm <sup>-1</sup> )   | Band Assignment                 |
| 2226   | CN stretching                   |
| 1606   | phenyl C-C stretching           |
| 1496   | phenyl C-C stretching           |
| 1460   | C-H deformation of pentyl chain |
| 1397   | C-H deformation of pentyl chain |
| 1378   | C-H deformation of pentyl chain |
| 1285   | C-H stretching of biphenyl ring |
| 1006   | phenyl C-H in-plane deformation |

Table 1

screen and timing diagram. The timing illustration is provided in the software screen to indicates the triggering and sampling times defined in the setup screen.

## RESULTS AND DISCUSSION

The results of performing an infrared static polarization measurement is illustrated in Figure 6. The top and middle spectra show parallel ( $A_{||}$ ) and perpendicular ( $A_{\perp}$ ) static dichroic measurements.

To evaluate the orientation of the liquid crystal within the cell, the intensity of the 5CB  $C\equiv N$  band at 2226  $cm^{-1}$  was used to calculate a dichroic ratio. A dichroic ratio

between 1.5 and 3.0 for this band indicates that there is a reasonable alignment of the liquid crystal within the cell. Table 1 lists the band assignments for

the 5CB molecule. The phenyl C-C bands have a similar orientation behavior as the  $C\equiv N$  bands in these dichroic spectra.

To verify the electrical conductivity of the liquid cell, 10 volts DC was placed across the cell electrodes. The bottom spectrum in Figure 6 shows the effect that the electric field has upon the parallel ( $A_{||}$ ) polarized spectrum. Performing the same measurement with perpendicular ( $A_{\perp}$ ) polarization reveals that the spectrum remains relatively unchanged.

These measurements indicate that the electric field reorients the 5CB alignment from their initial positions, aligned with the surface treatment of the cell windows, to a direction that is coincident with the direction of the applied electric field. Also, these polarization measurements confirm the integrity of the liquid crystal cell for orientation and electrical conductivity. With these criteria satisfied, step-scan time-resolved dynamic measurements were performed upon the liquid crystal cell

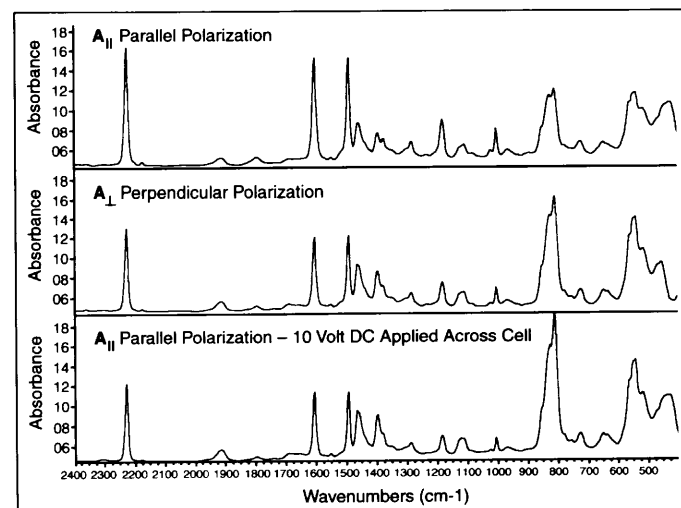


Figure 6: Static polarization spectra of oriented 5CB liquid crystal

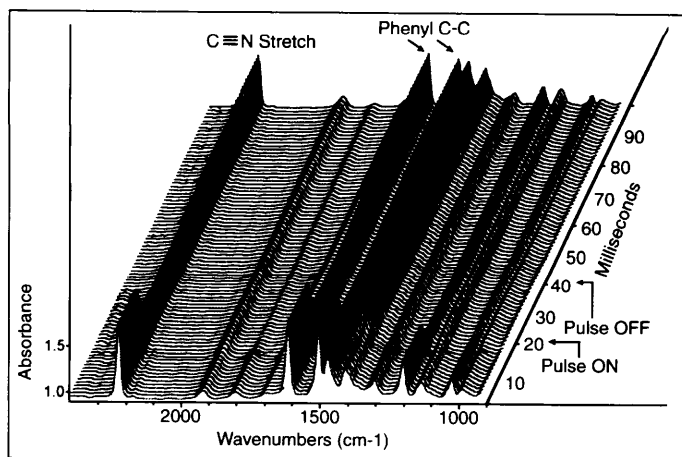


Figure 7: Dynamic Step-scan Time-resolve Spectra of the electrochemical response of 5CB liquid crystal molecules

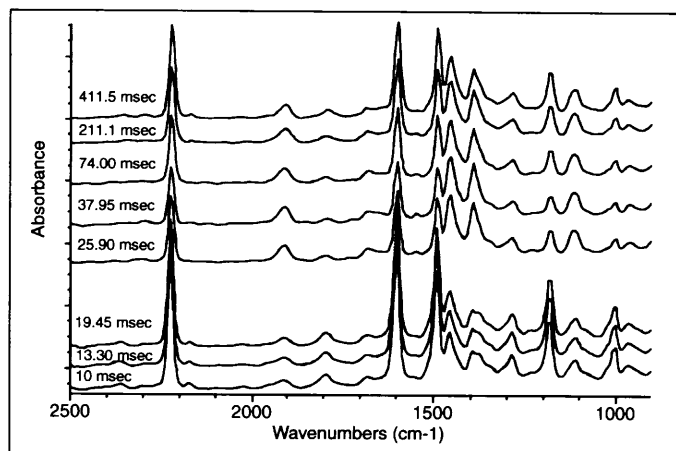


Figure 8: Selected time-slice spectra from a logarithmic dynamic step-scan time-resolve experiment of the electrochemical response of 5CB liquid crystal molecules

with the polarizer passing parallel ( $A_{||}$ ) infrared radiation through the sample cell.

The dynamic step-scan time-resolve measurement was performed using both the linear and logarithmic data acquisition methods. Figure 7 illustrates a waterfall plot of 100 – 1 millisecond dynamic step-scan time-resolve spectra of the electrochemical response of 5CB liquid crystal molecules. From the plot it can be observed that no reorientation occurs until the pulse generator bias is triggered at 20 milliseconds. The pulse bias remained on for a duration of 20 milliseconds.

From 40 milliseconds, when the bias is turned off, it can be observed in the subsequent spectra that the reorientation of the molecule to the original state occurs at a much slower rate than during the application of the voltage pulse. The last time-slice sampled in this experiment occurs at 60 milliseconds after the bias has been removed from the liquid cell and indicates that further time is required for the molecule to reorient to its original state.

To accommodate for a longer temporal sampling experiment, a logarithmic time base experiment was performed. This data collection scheme provided the advantage of sampling the initial portion of the orientation at a high sampling rate, followed by an increasing time separation as the reorientation progressed. Figure 8 illustrates several selected time-slice spectra from a logarithmic dynamic step-scan time-resolve experiment of the electrochemical response of 5CB liquid crystal

molecules. The spectra represent 1 millisecond time samples taken before, during and after the voltage bias pulse. The temporal sampling in this experiment occurred until a time of 425 milliseconds.

Utilizing the spectral processing tools in the Research OMNIC software, information on the reorientation dynamics of these logarithmic time-base spectra can be extracted. A spectral region of interest was selected and the peak-height of a band was computed for every spectral time-slice. Figure 9 illustrates a  $C\equiv N$  band ( $2226\text{ cm}^{-1}$ ) height versus time plot from a logarithmic dynamic step-scan time-resolve experiment of the electrochemical response of 5CB liquid crystal molecules. The plot shows that the orientation occurs quickly on the onset of the bias voltage and is a gradual process to the original state when the bias pulse is switched off.

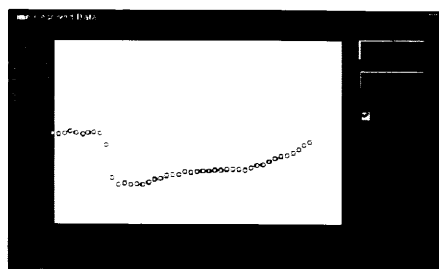


Figure 9:  $C\equiv N$  band ( $2226\text{ cm}^{-1}$ ) height versus time plot from a logarithmic dynamic step-scan time-resolve experiment of the electrochemical response of 5CB liquid crystal molecules

## CONCLUSIONS

This note demonstrates the utility of Nicolet's step-scan time resolved spectroscopy (TRS) package for the Magna-IR 860 E.S.P.

research FT-IR spectrometer in the measurement of the dynamics of liquid crystal reorientation studies. Step-scan time-resolve spectroscopy presents the researcher a spectroscopic probe which can measure kinetic events that occur in a time-frame that is temporally short for conventional rapid-scanning FT-IR spectroscopy.

The temporal dynamics of the liquid crystal molecule show that the applied electric field pulse reorients the 5CB alignment in a direction that is coincident with the direction of the applied electric field. This example measurement is a cyclic electrochemical type reaction.

It should be noted that researchers can also use this step-scan capability to measure other transient phenomena such as light induced chemical reactions (photocyclic reactions), gas-phase photodissociation/association reactions, and laser emission experiments.

## REFERENCES

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