Applications of Rapid Scan Data Collection

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KEYWORDS

FT-IR/chemicals, polymers/gas, liquids/ HATR, fiber optics, gas cell/kinetics, rapid scan

INTRODUCTION

Rapid scan techniques allow one to record infrared spectra quickly and accurately in kinetic events such as photochemical reactions, temperature or pressure jump, flowing liquids or diffusion kinetics, fast reactions between ions and oxidation-reduction processes. Rapid scan data collection software permits the study of events occurring in a very short time interval ranging from a few milliseconds to several hundred milliseconds. The spectral changes observed in this short time scale allow one to investigate the involved system.

Sampling Parameters

The time resolution and number of scans per second provided in the rapid scan experiment depend upon several factors including the velocity of the interferometer's moving mirror and the desired spectral resolution for the experiment. Utilizing the rapid scan velocities and spectral resolutions shown in Table 1, the corresponding temporal resolution and number of scans per second are provided by the Nicolet Magna-IR® spectrometer.

Table 1: Rapid Scan Performance of Magna-IR Spectrometers

Spectra/Second (Time Resolution in milliseconds)				
Resolution (cm^{-1})	5.06 cm/sec (80kHz)		8.22 cm/sec (130kHz)	
32	51.5	(19.4)	62.6	(16.0)
16	38.7	(25.8)	50.1	(20.0)
8	25.8	(38.8)	35.8	(27.9)
4	14.8	(67.6)	23.4	(42.7)
2	8.4	(119.0)	13.1	(76.3)

Table 1 shows that the fastest rapid scan data collection occurs at 32 cm^{-1} resolution with a moving mirror velocity of 8.22 cm/sec with over 62 scans per second collected with a time resolution of 16.0 milliseconds between scans. As we increase spectral resolution, the travel distance of the moving mirror increases and thereby reduces temporal resolution of the rapid scan experiment. In the rapid scan experiment we must match the required spectral and temporal resolutions for the experiment.

Gas Phase Spectra

For gas-phase studies, it may be necessary to separate overlapping absorbance bands or visualize the rotational spectra of the gas molecules. A spectral resolution on the order of 2-4 cm^{-1} may be required for gas phase spectra. Figure 1 shows an ethylene gas spectra collected at different spectral resolutions using the Magna-IR spectrometer and an MCT-A detector. These spectra were collected in the rapid scan data collection mode using a single scan.

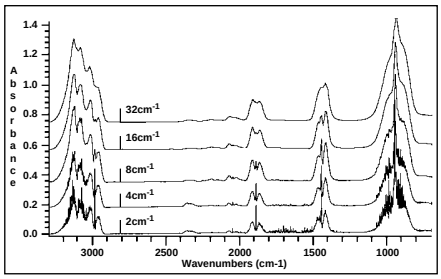

Figure 1

The fine structure of the spectra at 2 and 4 cm^{-1} resolution are readily apparent due to the rotational absorptions of the gas molecules. At the lower spectral resolution of 8 cm^{-1} some rotational absorptions are visible. However, at 16 or 32 cm^{-1} resolution virtually no fine structure is apparent.

Condensed Phase Spectra

In condensed phase spectra, higher spectral resolution is generally not required. Figure 2 shows a comparison of the effect of differing spectral resolutions for liquid-phase spectra of ethanol mixed with acetone (V/V=1:1) recorded in a Circle Cell®.

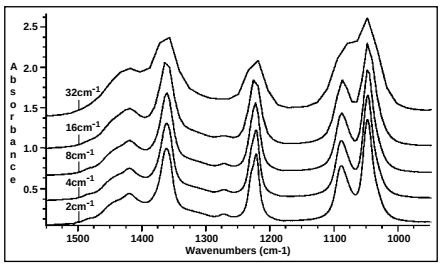

Figure 2

From the bottom spectrum measured at 2 cm^{-1} resolution to the 2nd to the top spectrum at 16 cm^{-1}, little difference in spectral resolution is observed. The two bands at 1050 and 1090 cm^{-1} in Figure 2 can be separated very well except at 32 cm^{-1} resolution. So in this example, for the best possible temporal resolution with minimal spectral resolution loss we would choose 16 cm^{-1} resolution for the rapid scan experiment.

Data Collection and Processing

For the rapid scan experiment, a stable, high-performance and versatile interferometer is required. A Fourier transform infrared instrument takes advantage of the fact that a complete single-sided scan of the interferometer mirror produces the entire bandwidth of spectral information. Utilizing the bi-directional data collection capabilities of the Magna-IR spectrometers, we can significantly increase the number of rapid scan spectra per second. In the bi-directional data collection mode, data are collected on forward and reverse mirror motions, which increases time resolution by nearly a factor of two.

Experimental setup for the rapid scan experiment is easy and straightforward with OMNIC® Series software. *Series Setup* and *Collect Series* in the OMNIC menu provide selection of rapid scan parameters and initiation of data collection. The time of rapid scan data collection is generally short – usually a few seconds. To synchronize the collection of rapid scan data with the experiment, the Magna-IR Start Accessory is recommended. This trigger mechanism sends a switch closure pulse to the experiment and simultaneously starts data storage via its I/O port connection between the optical bench and computer.

The Series data from the rapid scan experiment consist of a number of spectra, sequential in time, stored automatically onto the hard disk of the PC. OMNIC Series software provides an efficient means of processing data and generating waterfall or contour displays of the data.

Liquid Phase Dispersion

Figure 3 shows a waterfall plot of rapid scan spectra from a drop of acetone dispersing across the surface of a horizontal ATR crystal. The experiment was performed with a DTGS detector and interferometer scanning at 5.06 cm/sec. Each plotted spectrum is a single scan collected at 16 cm^{-1} resolution.

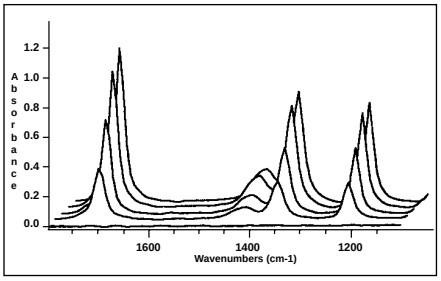

Figure 3

The total time shown in the waterfall display is 129 milliseconds, with 25.8 milliseconds between scans. At this rate of rapid scan data collection, we characterize the increased absorption of the acetone bands as the crystal surface becomes more fully covered. We see in this example that even using the DTGS detector operating at the high scan velocity of the rapid scan data collection, we produce excellent spectral stability and signal-to-noise ratio.

Chemical Reaction

The rapid scan spectra in Figure 4 were collected as a result of the reaction of KOH with isobutyric acid. Spectra-Tech's FiberLink™ mid-IR fiber optic sampling accessory was positioned in the main sample compartment of the Magna-IR spectrometer. The FiberLink's flexible 1.5 meter fiber optic cable was fitted with an ATR Needle Probe™ and extended from the FT-IR sample compartment to the reaction vial. Spectra were collected at 16 cm^{-1} resolution with an MCT-A detector. After a background single beam spectrum was collected through the ATR Needle Probe, its tip was immersed into 4 milliliter of 1.0 M isobutyric acid in D2O solution in a small vial. Then 4 milliliter of 1.0 M KOH in D2O was added into the vial simultaneous with the triggering of the rapid scan data collection. The reaction produces potassium isobutyrate and H_2O.

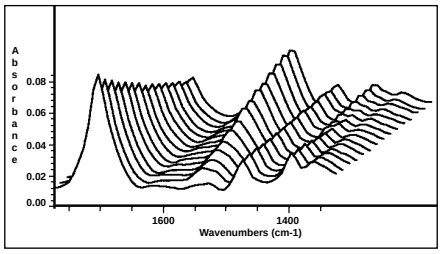

Figure 4

The intensities of the band at 1707 cm^{-1} ascribed to the C=O stretching vibration and the band at 1397 cm^{-1} mostly ascribed to O-H in-plane bending vibration in isobutyric acid decrease continuously. The intensities of the bands at 1416 and 1548 cm^{-1}, attributed to symmetric and asymmetric stretching vibration of the COO- group in the salt, increased continuously with the addition of KOH solution. The 15 spectra in Figure 4 were collected during 0.388 second interval, with 25.8 milliseconds between scans. Clearly, the rapid scan data collection defines the reaction progress and could be used to determine kinetics constants.

Gas Phase Mechanics

In Figure 5, we measured the rate of filling for an evacuated 10 meter gas cell. At 16 cm^{-1} resolution with an MCT-A detector and scanning at a rate of 8.22 cm/sec, we produced over 50 individually stored spectra per second with a 20 millisecond time resolution.

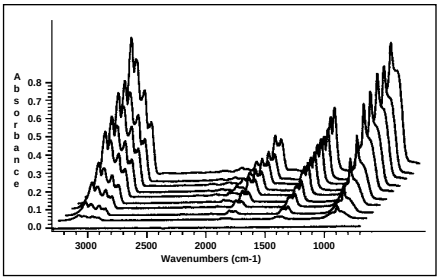

Figure 5

The scan in the foreground of the Waterfall display was collected just before the ethylene gas began to enter the gas cell from its reservoir. Subsequent spectra in the Series data file showed a plateau as the pressure equilibrated between the gas cell and its reservoir.

CONCLUSION

Rapid scan data collection provides a means for the kinetic measurement of fast changing chemical information. Time resolution to a few milliseconds is available for non-elastic experiments. Data collection parameters may be optimized based upon experimental requirements. Gases, liquids and solids may be measured in the rapid scan mode utilizing a variety of sampling accessories.

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