Development of a Time-Resolved FTIR System

Cheng K¹, Fan W.Y²

Department of Chemistry, Faculty of Science, National University of Singapore
3 Science Drive 3, Singapore 117543

An early triumph of time-resolved spectroscopy was the demonstration (by cine photography) that all four legs of a horse leave the ground when it gallops. To be able to investigate processes, which exist on the nano to femtoseconds time scales, it would reveal information, that will be of fundamental importance to physics, chemistry and biology. Time-resolved spectroscopy techniques are a powerful means of studying materials, giving information about the nature of the excitations, energy transfer, molecular motion, and molecular environment, information that is not available from steady-state measurements. This paper details the setting up and testing of a commercial FTIR spectrometer with time-resolved capability.

INTRODUCTION

Fourier transform infrared (FTIR) spectroscopic techniques have revolutionized the field of infrared chemical analysis by being able to produce high resolution spectra in a smaller time frame than traditional dispersive spectroscopy techniques.

One of the main disadvantages of traditional methods of producing a spectrum is the slowness of the process, as each point of the spectrum has to be recorded individually. This is also very inconvenient as it meant that the whole spectrum would need to be swept through even though only one or two peaks are of interest. However the development of Fourier Transform (FT) spectroscopy allows simultaneous and almost instantaneous recording of the whole spectrum.

The heart of a commercial FTIR spectrometer is the Michelson interferometer as shown in Fig. 1. It consists of a beamsplitter, a fixed mirror and a moving mirror. The collimated IR beam is split by the beamsplitter. 50% of the splited beam will be transmitted to the moving mirror that is moving at constant velocity, and the other 50% is reflected to the fixed mirror. The reflected beams (from the 2 mirrors) will then interfere constructively or destructively, depending on the wavelength of the light and the optical path difference between the mirrors. This pattern of interference is known as an interferogram. Fourier Transform converts the interferogram, which is an intensity vs time plot, into an intensity vs frequency plot. This type of scans is also known as linear scans.

¹ Student
² Asst. Prof.
FTIR is able to have a considerably shorter scanning time for a spectrum as compared to traditional dispersive method is because FTIR is able to obtain the whole spectrum across the entire frequency range at once. Whereas in dispersive IR, not only does each individual point needs to be recorded separately, the dispersive grating needs to be changed during the scan, as one grating is usually not enough to cover the entire frequency range.

For kinetic studies, FTIR is not insufficient by itself because linear scan works well for routine measurements but not for time-dependent processes occurring on 20 ms or faster time scales. Therefore for studies such as photochemistry where kinetics are in the micro and nanoseconds range, a technique, which is faster, would be needed.

A FTIR spectrometer with step-scanned ability will be able to carry out time-resolved studies in the micro to nanoseconds range. In a step-scan experiment, the moving mirror, instead of moving at a constant velocity as it would in a linear scan, is moved incrementally in steps. Data are collected at each mirror position. Therefore for photochemistry studies where a laser pulse is used in triggering a reaction. The spectrometer can be triggered to the laser and whenever the mirrors are moved to a new position, the laser will be triggered to fire a shot. Thus at each mirror position, data can be obtained up to the nanoseconds time range. This will be repeated until the moving mirror has gone through the entire movable distance and well-characterized time-resolved interferograms of the transient species will be obtained. The interferogram will then be converted by Fourier Transform to give spectra in the pre-determined time scales.

A test is carried out on the time-resolved capability of the FTIR spectrometer by employing a supersonic jet to simulate the appearance of the transient species.

**EXPERIMENT**

A schematic diagram of the experimental layout is shown in Fig. 2. The ThermoNicolet Nexus 870 FTIR spectrometer has its IR beam coupled out and guided by the use of gold mirrors. The beam is made to pass through the supersonic jet before entering back into the spectrometer. The spectrometer is triggered to a digital delay generator (DDG), which is then triggered to the supersonic jet controller. The jet is connected to a vacuum system which is capable of achieving ~10^{-6} Torr.
When the experiment starts, the spectrometer will send a trigger signal to the DDG every time the moving mirror is in a new position. The trigger signal will cause the jet controller to open the jet orifice for a pre-determined time. The gas that is released will traverse from the orifice to the vacuum pump. The molecules which are traveling at supersonic speed will be used to simulate the appearance of transient species and the IR beam which is passing through the jet will then detected the molecules. Fig. 3. shows the schematic of the supersonic jet.

**RESULTS**

OCS and N₂O gas were used for the testing but due to space constraint, only the OCS spectra is shown. The selected spectra shown in Fig. 3 shows that the spectrometer is able to detect the gaseous molecules.
The peak at ~ 2062 cm\(^{-1}\) is the O-C stretching frequency of OCS. The peak first appears at 450.0 us before reaching a maximum at 950.0 us. This shows that the spectrometer is able to detect the OCS molecules emerging from the jet. The reason why the peaks only started showing after 450.0 us could be due to the inertial effect that the high pressure (2 bar) that the gases exert on the opening gate of the orifice, thus preventing the orifice to be delayed.

CONCLUSION
The test is successful as it shows the ability of the spectrometer in detecting the gaseous molecules emulating transient species. Future projects will employed the spectrometer to be used in photokinetic studies where a pulsed laser would be used to initial a photolytic reaction.

ACKNOWLEDGEMENTS
I would like to thank my supervisor Dr Fan Wai Yip for being so gracious and patient with me, always willing to guide and even lent a listening ear. To Mr Li Peng\(^1\) who is ever so helpful and to my all laboratory mates who have help to prevent laboratory work from being a drudgery.

REFERENCES

\(^1\) PhD. candidature