Real-time sampling electronics for double modulation experiments with Fourier transform infrared spectrometers

Michael J. Green, Barbara J. Barner, and Robert M. Corn

Department of Chemistry, University of Wisconsin, 1101 University Ave., Madison, Wisconsin 53706

(Received 17 December 1990; accepted for publication 13 February 1991)

A novel synchronous real-time analog sampling method for obtaining the sum and difference interferograms in double modulation Fourier transform infrared absorption experiments is described, and the application of this sampling methodology to polarization-modulation FTIR measurements of thin films at metal surfaces is demonstrated. A quadratic approximation of the background signal is used to calculate the difference interferogram. The demodulation of a test waveform with the real-time sampling electronics reveals how the bandwidth limitations of previous double modulation experiments on FTIR interferometers that employed lock-in amplifiers have been eliminated.

I. INTRODUCTION

Double modulation spectroscopy is a general method for obtaining the differential absorption spectrum of a sample. For example, infrared reflection-absorption spectroscopy (IRRAS) of molecules adsorbed onto metal surfaces has been performed with the polarization modulation experiment schematically depicted in Fig. 1. In the traditional double modulation scanning experiments [Fig. 1(a)] the polarization of the light incident on a sample is modulated at a frequency \( \omega_1 \) between p-polarized light (light polarized parallel to the plane of incidence) and s-polarized light (light polarized perpendicular to the plane of incidence) with a photoelastic modulator (PEM) to obtain the differential reflectance spectrum, \( \Delta R/R \):

\[
\frac{\Delta R}{R} = \frac{I_p - I_s}{I_p + I_s},
\]

where \( I_p \) is the infrared spectrum obtained with p-polarized light and \( I_s \) the infrared spectrum obtained with s-polarized light. Since only p-polarized light has an appreciable amplitude at the metal surface (for a high angle of incidence), the differential reflectance spectrum provides a direct measurement of the vibrational spectrum of the adsorbed molecules without the need for a background reference. In a scanning experiment, the intensity of the source is modulated by a chopper at frequency \( \omega_2 \) simultaneously with the modulation of the polarization at \( \omega_1 \) to eliminate any background radiation. The polarization modulation frequency is typically 74 kHz, while the chopper frequency is typically \(< 1 \text{ kHz} \). As long as these two frequencies are well-separated, lock-in amplifiers referenced to \( \omega_1 \) and \( \omega_2 \) can be used to measure \((I_p - I_s)\) and \((I_p + I_s)\) very accurately and the differential reflectance spectrum can be obtained as a function of wavelength as the monochromator is scanned.

In polarization-modulation Fourier transform infrared reflection-absorption (PM-FTIRRAS) measurements [Fig. 1(b)] this separation of frequencies is much more difficult. The spectral information of the interferometric experiment is contained in a bandwidth of frequencies typically ranging from several hundred to 20 kHz, and the polarization modulation spectrum is centered about 74 kHz. The resultant waveform is the sum of an average...
interferogram signal plus an additional modulation due to the PEM with an amplitude that is a function of mirror position. For example, the central region of a PM-FTIRRAS interferogram from a Cr-coated Si wafer with a thin (20 nm) film of polyimide is shown in Fig. 2. The polarization modulation of the interferogram at a frequency of 74 kHz is readily observable on the infrared signal. Most commercial lock-in amplifiers have a minimum time constant of about 0.5 ms and are thus unable to follow the rapid variations of the modulation amplitude in this experiment. To avoid this problem, the moving mirror of the infrared interferometer is usually slowed down to lower the bandwidth characteristics of the average interferogram to below 2 kHz, permitting the use of a lock-in amplifier. This article describes a synchronous sampling method that we have recently implemented to obtain the differential reflectance spectrum from the polarization-modulated interferogram at normal mirror velocities. The method samples the input waveform \( V_{in} \) three times during each PEM modulation cycle to obtain an average \( V_{avg} \) and a difference \( V_{dif} \) interferogram that can be transformed and then ratioed to obtain the differential reflectance spectrum.

II. EXPERIMENTAL CONSIDERATIONS

The interferogram and FTIR spectrum shown in this article were obtained with a Mattson Cygnus 100 FTIR spectrometer at a nominal resolution of 2 cm\(^{-1}\). Polarization modulation of the infrared beam was obtained at a frequency of 74 kHz with a Hinds ZnSe photoelastic modulator. Further details of the optical components, the interface of the electronics to the spectrometer, and the preparation of the polyimide thin film sample have been given previously. All voltage waveforms were obtained with a 125 MHz digital oscilloscope (LeCroy Model 9400).

III. METHODOLOGY

Figures 3 and 4 show a block diagram and timing scheme for the demodulator circuit that produces \( V_{avg} \) and \( V_{dif} \) from \( V_{in} \). The circuit consists of five high quality (Crystal CS3112) video sample and hold amplifiers (pen-

\[
V_d(n) = V_p(n) - W_1 V_s(n) - W_2 V_s(n-1)
\]

FIG. 3. Block diagram for the demodulation electronics. The circuit converts a double modulation waveform \( V_{in} \) into the average and difference waveforms \( V_{avg} \) and \( V_{dif} \). Pentagons represent the synchronous sample-and-hold amplifiers, and are labeled according to when they are sampled during each modulation cycle. Squares in the diagram refer to gain or attenuation elements, and circles with the enclosed "\( \Sigma \)" refer to sum/difference amplifiers. The sign for each incoming signal to a sum/difference amplifier is shown at the inputs. Both \( V_{avg} \) and \( V_{dif} \) are sent through low pass filters to suppress any spurious high frequency modulation that is generated in the sampling process.
FIG. 6. Estimate of the modulation peak amplitude $V_d(n)$. $V_d(n)$ is obtained at the end of the modulation cycle from the three voltages $V_p(n)$, $V_x(n)$, and $V_x(n-1)$.

time during the modulation cycle at which the peak modulation signal occurs ($V_p$). The time at which $V_p$ is measured is the same for each cycle, and is adjusted at the beginning of an experiment after an examination of the corrected signal on an oscilloscope.

At the end of each PEM cycle an estimate of the modulation amplitude, $V_bkg$, is made. For the $n$th cycle, the estimate $V_bkg(n)$ is obtained from three sampled voltages: $V_p(n)$, $V_x(n)$, and $V_x(n-1)$ (see Fig. 6). This last voltage, $V_x(n-1)$, is the voltage obtained at the end of the previous cycle, and is held in an additional sample and hold circuit "h" as shown in the block diagram and timing scheme (Figs. 3 and 4). Just prior to the acquisition of $V_x(n)$, the voltage held from the previous cycle, $V_x(n-1)$, is transferred to circuit "h."

Fractions of the two voltages $V_x(n)$ and $V_x(n-1)$ are subtracted from $V_p(n)$ in order to provide a better estimate of $V_d(n)$:

$$V_d(n) = W_1 V_x(n) - W_2 V_x(n-1),$$

where $W_1$ and $W_2$ are the weighting factors. As seen in Fig. 6, if $V_p(n)$ alone were used as an estimate of the modulation amplitude (i.e., if only the subtraction $V_x$ from $V_p$ were considered), the background correction would be incorrectly approximated. This is because $V_bkg$, the interferogram in the absence of polarization modulation, has changed from the time $V_x(n)$ was obtained to the time when $V_p(n)$ was acquired. If $t_p$ is defined as the time at the beginning of the modulation cycle, $t_p$ as the time during the modulation cycle when $V_p(n)$ is obtained, and $t_x$ as the time at the end of the modulation cycle when $V_x(n)$ is acquired, then the value of the background at time $t_p$ can be estimated from $V_x$ at time $t_x$ by a series expansion:

$$V_{bkg}(t_p) = V_x(t_x) + V_{bkg}(t_x) \Delta t_p + V_{bkg}(t_x)(\Delta t_p)^2/2 + \ldots,$$

where $\Delta t_p = t_p - t_x$ and $V_{bkg}(t_x)$ and $V_{bkg}(t_x)$ are the first and second derivatives of $V_{bkg}$ evaluated at $t_x$. For the $n$th
FIG. 7. Test double modulation waveform for the real-time sampling electronics. (a) Combination waveform with 2 kHz sine wave background and a small amplitude “stepped” modulation. (b) The test stepped modulation waveform without the background.

cycle, the measurement of $V_{\text{bkg}}$ at $t_2$ is $V_s(n)$, and the two derivatives can be approximated by:

$$V'_{\text{bkg}}(t_2) \approx \frac{[V_s(n) + V_s(n - 1)]}{2\Delta t},$$  \hspace{1cm} (5)

$$V''_{\text{bkg}}(t_2) \approx \frac{[V_s(n) - V_s(n - 1)]}{\Delta t^2},$$  \hspace{1cm} (6)

where $\Delta t = t_2 - t_1$. From Eqs. (5) and (6) it can be shown that in order to correctly estimate the background to second order the weighting factors must be given by:

$$W_1 = \frac{1}{2} \left( \frac{\Delta t_2}{\Delta t} + \frac{\Delta t_1}{\Delta t_1} \right),$$  \hspace{1cm} (7)

$$W_2 = \frac{1}{2} \left( \frac{\Delta t_2}{\Delta t} - \frac{\Delta t_1}{\Delta t_1} \right).$$  \hspace{1cm} (8)

For example, if the peak measurement is made exactly in the middle of the modulation cycle, then $W_1 = 0.375$ and $W_2 = 0.125$. For the polarization-modulation interferograms used in the differential reflection-absorption measurements a quadratic background correction was sufficient to eliminate any leakage of the background voltage $V_{\text{bkg}}$ into the difference signal waveform. Higher order corrections could have been added onto $V_d(n)$ by using additional sample and hold circuits to store more previous measurements of $V_s$. Because the calculation of $V_d(n)$ requires the voltage $V_s(n)$ acquired at $t_p$, the difference signal $V_{\text{dif}}$ will be delayed in time by half a modulation cycle from when it occurs at $t_p$.

The difference signal $V_{\text{dif}}$ is created from the voltage waveform $V_d$ by filtering to remove any high frequencies introduced in the sampling. Concurrently the input voltage $V_{\text{in}}$ is filtered in a similar fashion to obtain the average voltage signal $V_{\text{ave}}$. Both signals are sent to FTIR spectrometer where they are digitized, transformed, and then ratioed to obtain the differential reflection-absorption spectrum.

IV. DEMODULATION PERFORMANCE TEST

To facilitate development and evaluation of the detection electronics, a double modulation test waveform generator was designed and constructed. The test waveform consisted of a 74 kHz pulse amplitude modulated signal superimposed upon a large 2 kHz sine wave background [Fig. 7(a)]. The 74 kHz modulation consisted of a repeated series of eight four-pulse sequences, each with a slightly larger amplitude [Fig. 7(b)]. Figure 8(a) plots the output signal $V_{\text{dif}}$ obtained by the real-time sampling electronics from the test waveform. Virtually no sine wave background appears in the difference signal. For comparison, Fig. 8(b) shows the response of an E.G.&G. Model 124A lock-in amplifier to the same input signal. Even though the lock-in was operated with its minimum output time constant, it is apparent from the figure that the lock-in is un-
able to recover the stepped waveform, whereas the real-time sampling electronics faithfully reproduces the eight-step amplitude modulation signal.

V. APPLICATION TO POLARIZATION MODULATION-FTIR EXPERIMENTS

The application of the real-time sampling electronics to PM-FTIRRAS experiments results in the accurate measurement of the differential reflection-absorption spectrum. For example, processing the PM-FTIRRAS waveform shown in Fig. 2 with the real-time sampling electronics leads to the two signals $V_{avg}$ and $V_{dif}$ shown in the figure. These "sum" and "difference" interferograms are sent to the spectrometer, digitized, and transformed to obtain the sum and difference spectra $I_{avg}(\omega)$ and $I_{dif}(\omega)$, respectively. The ratio $I_{dif}/I_{avg}$ yields the differential reflectance spectrum $\Delta R/R$ times a weighting term that results from the variation of the PEM modulation efficiency as a function of wavelength. Figure 9(a) plots the ratio $I_{dif}/I_{avg}$ for a PM-FTIRRAS experiment where the PEM was nominally set for most efficient modulation at 5.50 µm (1818 cm$^{-1}$). Normalization of the ratio by this weighting term results in the spectrum shown in Fig. 9(b). In a previous paper, it was demonstrated that the real-time sampling electronics can provide sufficient sensitivity to obtain the differential reflectance spectrum from monolayers at metal surfaces.

In addition to metal surfaces, the demodulation electronics described in this paper can in principle be applied to a variety of PM-FTIRRAS measurements. For example, infrared vibrational circular dichroism measurements result in a similar modulated interferogram, and the synchronous sampling electronics could be applied directly to such systems. Other double modulation FTIR experiments to which the real-time sampling electronics could be applied are linear dichroism in stretched polymer films, photodeflection measurements, and attenuated total reflection (ATR) geometries.

ACKNOWLEDGMENTS

This work was supported by grants from the National Science Foundation and the Wisconsin Alumni Research Foundation (WARF).