Dynamic Infrared Spectroscopy Using the Rapid-Scan Technique

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A technique using rapid-scan Fourier transform infrared (FT-IR) spectroscopy to observe reversible dynamic changes of systems under an externally applied perturbation is introduced. The technique does not require a lock-in amplifier or synchronization between the applied perturbation and the spectral acquisition. With the use of a carefully designed sampling rate with respect to the perturbation period and reconstruction of the observed spectral intensities, dynamic spectral intensities of the system are obtained. Due to the repeated behavior, the reconstructed spectral intensities can be used to represent the dynamic characteristic of the system. The experimentation time of the rapid-scan technique is significantly shorter than that of the step-scan technique. The influences of noise and experimental parameters on the observed spectral intensities are verified. Applications of the technique to systems with sinusoidal dynamic changes and exponentially decaying dynamic changes are demonstrated.

Index Headings: Fourier transform infrared spectroscopy; FT-IR spectroscopy; Dynamic infrared spectroscopy; Rapid-scan technique; Step-scan technique.

INTRODUCTION

In a system where dynamic changes, such as orientation and relaxation of molecules, are induced by an externally applied perturbation, chemical species in the system respond to the perturbation differently according to their structural characteristics and environments.¹ Fourier transform infrared (FT-IR) spectroscopy with polarized radiation is a powerful tool for the observation of such changes since it is sensitive to the orientation of selected functionality with respect to the polarization axis. For a system with fast and reversible dynamic changes (i.e., those with a period of a millisecond or less), step-scan FT-IR spectroscopy can be applied. By taking advantage of the repeatable characteristics of the system and step displacement of the moving mirror, the step-scan technique offers time-dependent spectra, high spectral resolution, and desirable signal-to-noise (S/N) ratio. If the rapid-scan technique is employed in such a system, the acquired spectra represent the average of changes during the scanning period. As a result, dynamic changes in the system may not be observed if the scanning period or scanning time is too long. There are unique approaches available to study such systems using both step-scan and rapid-scan techniques.¹⁻⁶

Some of the limitations of the step-scan technique are the requirement of special accessories (i.e., lock-in amplifiers) and complex experimental setup. With the *very* fast scanning capability of available spectrometers and powerful computers, by using a carefully designed sampling rate in conjunction with the perturbation period, the rapid-scan technique can do the same job as does the step-scan technique when it is used to observe phenomena occurring in the subsecond time frame. The purpose of this paper is to introduce an application of rapid-scan FT-IR spectroscopy to observe dynamic changes of reversible phenomena without using a lock-in amplifier and without synchronization between the externally applied perturbation and spectral acquisition.

THEORY

The Observed Spectral Intensity. When a system is subjected to an externally applied perturbation, chemical species in the system respond to the perturbation differently according to their structural characteristics and environments. The dynamic changes of those species may be monitored via infrared spectra at the characteristic frequencies.^{1,7,8} If the changes are reversible and are proportional to the magnitude of the applied perturbation, the perturbation can be repeated in order to observe the same phenomena again. With repetition of the perturbation, dynamic changes of the system at different magnitudes of perturbation can be observed and/or those at the same magnitude can be observed again in order to improve the S/N ratio. The external perturbations can be any kind (i.e., mechanical, electrical, or chemical) and may take any waveform (i.e., sinusoidal, step, or exponential decay). Analogous to the step-scan technique, the following method shows an application of the rapid-scan technique for observation of repeatable phenomena.

In general, the time-dependent spectral intensity at frequency ν can be expressed as²

$$A(v, t') = \bar{A}(v) + \bar{A}(v, t') = \bar{A}(v) + \bar{A}(v)F(v, t') \quad (1)$$

where t' is the time defined with respect to the perturbation domain, A(v, t') is the time-dependent spectral intensity, $\overline{A}(v)$ is the static spectral intensity, $\widetilde{A}(v, t')$ is the perturbation-induced dynamic spectral intensity, $\widehat{A}(v)$ is the coefficient of the dynamic change, and F(v, t') is the dynamic function or wave form of the dynamic. The above equation can be applied to an experimental setup only where the external perturbation and the spectral acquisition are synchronized (i.e., perturbation and spectral acquisition are started at the same time).

In the case where the applied perturbation is not synchronized with the spectral acquisition, the perturbationinduced dynamic spectral intensity can be expressed as (see Fig. 1)

$$\tilde{A}(\mathbf{v}, t') = \hat{A}(\mathbf{v})F(\mathbf{v}, t + \tau')$$
(2)

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FIG. 1. Schematic illustration for spectral acquisition without synchronization of the external perturbation and spectral acquisition. The solid line (**A**) shows the magnitude of the perturbation, the dotted line (**B**) shows the changes in spectral intensity as a result of the perturbation, and the square symbol indicates the acquired spectrum at time t_i . In practice τ' and τ are unknown parameters. A schematic illustration for spectral reconstruction or spectral mapping into the first perturbation cycle using the observation time and perturbation period is shown in **C**.

where t is the time defined with respect to the spectral acquisition domain; τ' is the time difference between the starting points of the perturbation and that of the spectral acquisition. Since the external perturbation has a period of T, the magnitudes of the perturbation and the dynamic changes of the system are repeated with a period equal to that of the external perturbation. As a result, Eq. 2 can be rewritten as

$$\tilde{A}(\mathbf{v}, t') = \hat{A}(\mathbf{v})F(\mathbf{v}, t + t_{\mathrm{m}} + \tau) = \hat{A}(\mathbf{v})F(\mathbf{v}, t + mT + \tau)$$

$$= A(\mathbf{v})F(\mathbf{v}, t+\tau), \qquad m = 0, 1, 2, 3, \dots$$
(3)

where τ is the delay time (i.e., the time difference between the start of measurement and the closest time t_m where the magnitude of the perturbation equals zero). Figure 1 shows a schematic illustration for an observation of a reversible phenomenon where the applied perturbation and spectral acquisition are not synchronized.

Since the rapid-scan technique is used, the observed spectral intensity is an average of the changes during the observation period (i.e., the scanning time for a spectrum). A spectral intensity acquired at time t with an observation period $\Delta t_{\rm obs}$ is given by

$$A_{\rm obs}(\mathbf{v}, t) = \frac{1}{\Delta t_{\rm obs}} \int_{t-\Delta t_{\rm obs}/2}^{t+\Delta t_{\rm obs}/2} A(\mathbf{v}, t) dt$$
$$= \bar{A}(\mathbf{v}) + \frac{1}{\Delta t_{\rm obs}} \int_{t-\Delta t_{\rm obs}/2}^{t+\Delta t_{\rm obs}/2} \tilde{A}(\mathbf{v}, t) dt \qquad (4)$$

where $A_{obs}(v, t)$ is the observed spectral intensity during the time interval

$$t - \frac{\Delta t_{\rm obs}}{2}$$
 to $t + \frac{\Delta t_{\rm obs}}{2}$.

The observed dynamic spectral intensity, $\tilde{A}_{obs}(v, t)$, is then defined as

$$\tilde{A}_{obs}(\mathbf{v}, t) = A_{obs}(\mathbf{v}, t) - \tilde{A}(\mathbf{v}) = \frac{1}{\Delta t_{obs}} \int_{t-\Delta t_{obs}/2}^{t+\Delta t_{obs}/2} \tilde{A}(\mathbf{v}, t) dt$$
$$= \frac{\hat{A}(\mathbf{v})}{\Delta t_{obs}} \int_{t-\Delta t_{obs}/2}^{t+\Delta t_{obs}/2} F(\mathbf{v}, t+\tau) dt.$$
(5)

Since the system is repeated at a period of T, spectral intensities within a single perturbation period can be used to represent the dynamic behavior of the system. By taking advantage of the repeated behavior, we can superimpose the observed dynamic spectral intensity sampling at time t into time t^1 in a single perturbation period by the following expression:

$$\tilde{A}_{obs}(\mathbf{v}, t) = \tilde{A}_{obs}(\mathbf{v}, kT + t^{1}) = \tilde{A}_{obs}(\mathbf{v}, t^{1})$$

$$k = 0, 1, 2, 3, \dots$$
(6)

where t^1 is the time defined within a single perturbation period (i.e., $0 \le t^1 \le T$). With the use of a carefully designed sampling rate with respect to the perturbation period, the observed time-dependent spectral intensities of the system within a single perturbation period can be reconstructed. The schematic illustration for spectral reconstruction is shown in Fig. 1.

In the following examples, systems with sinusoidal dynamic behavior and exponentially decaying dynamic behavior are examined since they are common perturbation waveforms and dynamic phenomena. It should be noted that there is no synchronization between the external perturbation and the spectral acquisition in the experimentally observed systems. The time for spectral reconstruction is the acquisition time of each spectrum, which can be obtained from the spectrometer. The perturbation period is used to map or project the spectrum acquired at a particular time into the first perturbation cycle.

Systems with Sinusoidal Dynamic Changes. An example of systems with this type of dynamic change is the orientation and recovery of polymer molecules under a small sinusoidal strain. The time-dependent total strain of such a system is given by^{1,4,5,7}

$$\mathbf{e}(t) = \mathbf{\bar{e}} + \mathbf{\tilde{e}}(t) \tag{7}$$

where $\epsilon(t)$ is the time-dependent total strain, $\bar{\epsilon}$ is the static strain, and $\tilde{\epsilon}(t)$ is the time-dependent dynamic strain. The time-dependent sinusoidal strain with a small amplitude $\hat{\epsilon}$ and a frequency f Hz (i.e., f = 1/T) can be expressed as

$$\tilde{\epsilon}(t) = \hat{\epsilon}\sin(2\pi f t) = \hat{\epsilon}\sin(\Omega t)$$
 (8)

where Ω is the angular frequency. If the amplitude of the applied strain is small (i.e., within the linear elastic region), a linear relationship between the magnitude of perturbation and the degree of orientation can be assumed.^{1,2,5} The time-dependent spectral intensity at frequency v is given in terms of the angular frequency by

$$\begin{aligned} A(\mathbf{v}, t) &= A(\mathbf{v}) + A(\mathbf{v}, t) \\ &= \bar{A}(\mathbf{v}) + \hat{A}(\mathbf{v}) \sin[\Omega(t+\tau) + \beta(\mathbf{v})] \end{aligned} \tag{9}$$



data mapped into a single perturbation period

FIG. 2. Schematic illustration for an observation of dynamic changes in a system under external perturbation with the rapid-scan technique. Spectra are acquired with an observation time of Δt_{obs} and a sampling interval of Δt_{samp} . (A) The magnitude of the applied perturbation. (B) The observed spectral intensity at frequency v as a function of acquisition time. (C) The spectral intensities in **B** mapped (or superimposed) into a single perturbation period.

where A(v) is the amplitude of the sinusoidal variation, and $\beta(v)$ is the phase angle of the dynamic change. It should be noted that $\overline{A}(v)$ in this case is simply the average spectral intensity. According to Eq. 5, the observed dynamic spectral intensity at time t is given by

$$\begin{split} \tilde{\mathcal{A}}_{obs}(\mathbf{v}, t) &= \frac{\hat{\mathcal{A}}(\mathbf{v})}{\Delta t_{obs}} \int_{t-\Delta t_{obs}/2}^{t+\Delta t_{obs}/2} \sin[\Omega(t'+\tau) + \beta(\mathbf{v})] dt' \\ &= -\frac{\hat{\mathcal{A}}(\mathbf{v})}{\Omega \Delta t_{obs}} [\cos[\Omega(t'+\tau) + \beta(\mathbf{v})]]_{t-\Delta t_{obs}/2}^{t+\Delta t_{obs}/2} \\ &= \frac{2\hat{\mathcal{A}}(\mathbf{v})}{\Omega \Delta t_{obs}} [\cos[\Omega \tau + \beta(\mathbf{v})] \sin(\Omega t) \sin(\Omega \Delta t_{obs}/2) \\ &+ \sin[\Omega \tau + \beta(\mathbf{v})] \cos(\Omega t) \sin(\Omega \Delta t_{obs}/2)] \\ &= \frac{\sin(\Omega \Delta t_{obs}/2)\hat{\mathcal{A}}(\mathbf{v})}{\Omega \Delta t_{obs}/2} [\cos[\Omega \tau + \beta(\mathbf{v})] \sin(\Omega t) \\ &+ \sin[\Omega \tau + \beta(\mathbf{v})] \cos(\Omega t)] \\ &= \sin(\Omega \Delta t_{obs}/2) \hat{\mathcal{A}}(\mathbf{v}) \sin[\Omega(t+\tau) + \beta(\mathbf{v})] \\ &= \hat{\mathcal{A}}_{obs}(\mathbf{v}) \sin[\Omega(t+\tau) + \beta(\mathbf{v})]. \end{split}$$

The above equation indicates that the observed dynamic spectral intensity has exactly the same dynamic function as that of the *true* perturbation-induced dynamic spectral intensity. The corresponding reconstructed spectral intensity within a single perturbation cycle of the observed spectral intensity at time t is given by



FIG. 3. The influence of observation time on the observed spectral intensities at frequencies v_1 (solid lines) and v_2 (dotted lines) with a perturbation period of 10 s: the true spectral intensities (top), the observed spectral intensities with $\Delta t_{obs} = 2$ s (middle), and $\Delta t_{obs} = 6$ s (bottom).

$$\tilde{A}_{obs}(\mathbf{v}, t^{1}) = \hat{A}_{obs}(\mathbf{v}) \sin[\Omega(kT + t^{1} + \tau) + \beta(\mathbf{v})]$$
$$= \hat{A}_{obs}(\mathbf{v}) \sin[\Omega(t^{1} + \tau) + \beta(\mathbf{v})].$$
(11)

In order to verify its applicability and limitation, the technique is applied to both simulated and experimentally observed spectral intensities. For the simulated system, the simulation parameters for sinusoidal dynamic changes are f = 0.1 Hz; delay time $\tau = 3$ s; true dynamic amplitudes $\hat{A}(v_1) = 0.10$ a.u. and $\hat{A}(v_2) = 0.15$ a.u.; and phase angles $\beta(v_1) = 0.2$ radian and $\beta(v_2) = 0.5$ radian. It should be noted that in the actual experiment only the perturbation frequency, sampling times, and observation period are known parameters. A schematic illustration for an observation of the changes of the systems is shown in Fig. 2. The spectral intensities are observed with various sampling intervals, Δt_{samp} , and observation periods, Δt_{obs} . The N observed spectral intensities are reconstructed (i.e., superimposed into a single perturbation period) in order to obtain the observed dynamic changes of the system. Figure 3 shows the effect of the observation period on the observed dynamic amplitudes. As the observation period gets longer, the observed dynamic amplitude becomes smaller. Figure 4 shows the examples of sampling intervals designed with respect to a perturbation period in order to obtain different numbers of reconstructed spectral intensities. The S/N ratio of the superimposed spectral intensity can be enhanced by taking advantage of the periodic characteristic of the system. Figure 5 shows the designed experimental parameters for obtaining reconstructed spectral intensities with various S/N ratios. By observing the system with a long observation time or by observing a large number of spectra and averaging spectral intensities of the same superposition time or combination, one can enhance the S/N ratio.

In the case of the experimentally observed system, a film $(30 \times 10 \times 0.025 \text{ mm})$ of 80:20 poly(dimethyl si-



FIG. 4. The design of sampling intervals with respect to the perturbation period (10 s) in order to obtain different numbers of sampling data after spectral reconstruction. In the case of a 9.0 s sampling period, the minimum time required for spectral collection in order to obtain the necessary number of data point to fill in a single perturbation cycle is $t_{\min} = 2 \times 5 \times 3 \times 3$ s. The number of data points is given by $t_{\min}/\Delta t_{\text{samp}}$, (A) The spectral intensity as a function of acquisition time, and (B) the spectral intensity mapped into a single perturbation cycle.

loxane)/polycarbonate copolymer is subjected to a sinusoidal perturbation (Rheometric Scientific RSA-2). The film is stretched with ~ 0.3% strain at 0.1 Hz. The spectra are observed in rapid-scan mode by using the rapid-scan time-resolved spectroscopy (Rapid Scan TRS) option of the OPUS software. A set of 101 transmission spectra is acquired with 10 scan coaddition at 4 cm^{-1} resolution by a Bruker IFS 66 FT-IR spectrometer equipped with an MCT detector. The output is a multi-file, which is a big file that contains all periodically observed spectra over the entire experiment. Each time-dependent spectrum with its observation time and observation period can be extracted from the multi-file by a home-written macro. Each spectrum has the same observation period. The observation time of each spectrum and the perturbation period (i.e., 10 s in this case) are used to reconstruct the dynamic behavior of the system within a single perturbation cycle (i.e., the first perturbation cycle). A schematic illustration of the experimental setup and a static spectrum of the film (nonpolarized radiation) are shown in Fig. 6.

Although the spectra show saturation in the region below 1300 cm⁻¹, the high-frequency region is still useful for observation of the dynamic behavior of the molecules under the perturbation. Figure 7A shows the amplitudes of the applied sinusoidal strain with respect to the acquisition time. Even though the observed signals (i.e., the time-dependent strains obtained from the perturbation source), show nonmeaningful features, the reconstructed signals exhibit sinusoidal behavior, as shown in Fig. 7B. Since some reconstructed signals provide redundant in-



FIG. 5. The influences of the observation period and the number of observed spectra on the S/N ratio of the reconstructed spectral intensities. Figures **A**–**C** show the enhancement of the S/N ratio by the number of acquired spectra with $\Delta t_{obs} = 1$ s and the number of acquired spectra of 100 (**A**), 300 (**B**), and 500 (**C**). Figures **D**–**F** show the enhancement by variation of observation period of 1 s (**D**), 3 s (**E**), and 5 s (**F**) on the same number of acquired spectra of 200. The assumed noise amplitude per one scan is 0.05 a.u. with an average scanning time of 0.2 s.

formation, averaging is applied in order to improve the S/N ratio (Fig. 7C). From the figure one will quickly notice that the perturbation magnitudes at the starting point of the measurements with p- and s-polarization are not the same. This result is due to the fact that both experiments have been performed independently. As a result, their perturbation signals or spectral acquisitions start at different perturbation magnitudes. For easy interpretation and direct comparison of the dynamic behavior from these two data sets, the reconstructed signals have to be modified. By taking advantage of the repetitive nature of the system, one can shift the time domain of the reconstructed signal in order to get a graphical illustration



FIG. 6. Schematic illustration for the experimental setup of the sinusoidal system (\mathbf{A}) and a static spectrum (no perturbation is applied) of the 80:20 poly (dimethyl siloxane)/poly(carbonate) copolymer (\mathbf{B}).



FIG. 7. The time-dependent magnitude of the sinusoidal perturbation (**A**); mapped time-dependent perturbation magnitude in a single perturbation cycle (**B**); average of the redundant signals or signals with common superimposed times (**C**); and time-shifted spectral intensities (**D**) in order to obtain perturbation cycles start with the same perturbation magnitude ($t_{shift} = 0$ s for *p*-polarization and $t_{shift} = 3.63$ s for *s*-polarization).

where the magnitudes of the perturbation at the beginning are the same. Figure 7D shows the time-shifted signals where the time domain in the s-polarization data set is shifted by 3.63 s (i.e., the observed data in the first perturbation cycle from $t^1 = 0$ s to $t^1 = 3.63$ s are moved forward by a period of the perturbation). Figure 8 shows the dynamic spectral intensities of the system at 1410 cm⁻¹ (the graphical illustrations are coincident with those in Fig. 7). There are two sources for intensity variations: molecular orientation and thickness change. An obvious difference between the magnitude of intensity variations of the p- and s-polarized spectral intensities indicates stretching-induced orientation since the thickness change due to stretching would induce an equal magnitude of intensity variations. According to Figs. 7D and 8D, there are significant delays between the time-dependent perturbation magnitude and the time-dependent spectral intensities. This discrepancy arises from the way the raw data are reported. The perturbation signals show stretching magnitude as a function of time, while the spectroscopic signals reveal spectral intensities with respect to the acquisition time, which is an average value over the observation period.

Systems with Exponentially Decaying Dynamic Changes. Examples of systems with this type of dynamic change are orientation and relaxation of low- and highmolecular-weight liquid crystals under the influence of an applied electric field.^{6,9,10} In general, the time-depen-



FIG. 8. Dynamic spectral intensity of the copolymer at 1410 cm⁻¹ under the influence of sinusoidal perturbation. Spectral intensities as a function of the acquisition time (A); intensities mapped into a single perturbation cycle (B); average of the intensities shown in **B** with a common superimposed time (C); and a time-shifted spectral intensity (**D**). For a direct comparison between two data sets, the spectral intensities with *s*-polarized radiation are shifted by 3.63 s.

dent spectral intensity during the relaxation phenomena is given by

$$A(v, t) = \bar{A}(v) + \tilde{A}(v, t) = \bar{A}(v) + \hat{A}(v)e^{-k(v)t}$$
(12)

where k(v) is the exponential decay constant at frequency v. The observed dynamic spectral intensity at time t with an observation time Δt_{obs} is given by

$$\tilde{A}_{obs}(\mathbf{v}, t) = \frac{\hat{A}(\mathbf{v})}{\Delta t_{obs}} \int_{t-\Delta t_{obs}/2}^{t+\Delta t_{obs}/2} e^{-k(\mathbf{v})t'} dt'$$

$$= \frac{\hat{A}(\mathbf{v})}{k(\mathbf{v})\Delta t_{obs}} \{e^{-k(\mathbf{v})[t-\Delta t_{obs}/2]} - e^{-k(\mathbf{v})[t+\Delta t_{obs}/2]}$$

$$= \frac{[e^{k(\mathbf{v})\Delta t_{obs}/2} - e^{-k(\mathbf{v})\Delta t_{obs}/2}]\hat{A}(\mathbf{v})}{k(\mathbf{v})\Delta t_{obs}} e^{-k(\mathbf{v})t}$$

$$= \hat{A}_{v}(\mathbf{v})e^{-k(\mathbf{v})t}, \qquad (13)$$

From Eqs. 12 and 13, one will quickly notice that the dynamic function of the observed spectral intensity is the same as that of the *actual* time-dependent spectral intensity. The shape of the observed dynamic spectral intensities deviates from that of the actual time-dependent intensities according to the observation period. The greater the observation period, the larger the deviation. The influence of the observation time on the observed dynamic spectral intensities is shown in Fig. 9.

Again, the sampling rate can be designed with respect



FIG. 9. The influence of the observation period on the observed spectral intensities with an exponentially decaying dynamic behavior. The magnitude of the perturbation in a single perturbation cycle (**A**). The true dynamic spectral intensities of the system with a decay constant k of 1.3 (**B**). The observed dynamic spectral intensities with $\Delta t_{obs} = 0.5$ s (**C**) and $\Delta t_{obs} = 2$ s (**D**).

to the perturbation period in order to obtain a good sampling of dynamic spectral intensities within a single perturbation period (i.e., Fig. 10). Unlike the sinusoidal case, this system consists of two phenomena, excitation and relaxation; therefore, the superimposed dynamic spectral intensities may not give a physically meaningful dynamic change depending on the delay time (i.e., Fig. 10B). By



FIG. 10. The influence of the delay time on the reconstructed dynamic spectral intensities. The observed spectral intensities as a function of acquisition time with $\Delta t_{samp} = 7.6 \text{ s}$ (**A**), the corresponding reconstructed spectral intensities (**B**), and the time-shifted spectral intensities (**C**). The perturbation period and decay constant are the same as those in Fig. 9 with $\Delta t_{obs} = 0.5 \text{ s}$. The delay time is 5 s. T_0 indicates an onset where only the exponentially decay dynamic behavior is observed (**C**).



FIG. 11. Schematic illustration for an experimental setup of the system with exponentially decaying dynamic behavior (A). A static spectrum of the liquid crystalline 5CB (B).

taking advantage of the periodicity of the system [i.e., $A_{obs}(v, t^1) = A_{obs}(v, t^1 + T)$], one can shift the time domain in order to obtain a meaningful dynamic change (i.e., Fig. 10C).

In the case where only the decay process is considered, the spectral intensity with an exponential decay dynamic change at frequency v is given by

$$\tilde{\mathcal{A}}_{obs}(\mathbf{v}, t^{1}) = \begin{cases} \hat{\mathcal{A}}_{obs} e^{-k(\mathbf{v})(t^{1}-t_{e})} & t^{1} \ge t_{e} \\ 0 & \text{otherwise,} \end{cases}$$
(14)

where t_e is the time when the exponential decay process starts (in practice t_e is not known). Care must be taken since the transition from excitation to relaxation is not clear if the observation period is too long.

Since the spectral intensities observed by the rapidscan technique are the averages of the changes during the observation period, it is more meaningful to use only the observed spectral intensities within the region that represents only the exponential decay process. If the range of *meaningful* observed spectral intensities is defined by $T_0 < t^1 < T$ (i.e., in the time-shifted spectral intensities where dynamic changes begin with the excitation process, Fig. 10C), the spectral intensities within the defined interval are independent of the delay time τ . As a result,



FIG. 12. Time-dependent spectral intensities in step-scan mode. The dynamic behavior of the liquid crystalline 5CB under the influence of the applied electric field observed at 1607 (A) and 2227 cm⁻¹ (B).



FIG. 13. Time-dependent spectral intensities in rapid-scan mode. The dynamic behavior of the liquid crystalline 5CB under the influence of the applied electric field observed at 1607 (**A**) and 2227 cm⁻¹ (**B**); their corresponding time-shifted spectral intensities are shown in **C** and **D**.

synchronization between spectral acquisition and perturbation is not required. The spectral intensity at time t^1 can be rewritten with respect to a new reference time T_0 as (i.e., T_0 is arbitrary):

$$\tilde{\mathcal{A}}_{obs}(\mathbf{v}, t^{1}) = \hat{\mathcal{A}}_{obs}e^{-k(\mathbf{v})(t^{1}-T_{0}+T_{0}-t_{e})} = \hat{\mathcal{A}}_{obs}e^{-k(\mathbf{v})(T_{0}-t_{e})}e^{-k(\mathbf{v})(t^{1}-T_{0})}$$

= $\tilde{\mathcal{A}}_{obs}(\mathbf{v}, T_{0})e^{-k(\mathbf{v})(t^{1}-T_{0})}$ (15)

where $\tilde{A}_{obs}(v, T_0)$ is the dynamic spectral intensity at $t^1 = T_0$, which can be obtained from the observed spectral intensities. The above equation indicates that dynamic spectral intensities within the selected region can be used to represent dynamic changes of the decay process.

The system under investigation is the orientation and relaxation of the liquid crystal 5CB under the influence of the applied electric field.9 The pre-aligned liquid crystal is perturbed by an applied electric field (± 10 V dc at a switching frequency of 10 kHz) with an excitation period of 215 ms and relaxation period of 600 ms. The transmission spectra are collected to 8 cm⁻¹ resolution with a Bruker IFS 28 FT-IR spectrometer equipped with an MCT detector. A schematic illustration of the experimental setup and a spectrum of the pre-aligned 5CB under p-polarized radiation are shown in Fig. 11. Due to the pre-aligned characteristic, changes in spectral intensity upon perturbation can be observed only with p-polarized radiation (i.e., with the electric field component of the radiation parallel to the rubbing direction of the polyimide orientation-induced layer). Spectral acquisitions in both step-scan and rapid-scan modes were performed. In the step-scan mode, the spectra were acquired during the first 500 ms of the perturbation period. A set of 500 spectra with time resolution of 1 ms were collected. In order to improve the S/N ratio, five consecutive step-scan spectra were averaged. The dynamic changes of the spectral intensity at 1607 and 2227 cm⁻¹ are shown in Fig. 12. In the rapid-scan mode, 500 consecutive spectra are collected with one scan coaddition (acquisition time for each spectrum is 95 ms) with the use of the Rapid Scan TRS spectral acquisition option of the OPUS software. The acquired spectra are then superimposed into a single perturbation period. Spectra with common superposition times are averaged in order to improve S/ N ratio (three spectra in this case). The dynamic changes of the system observed by rapid-scan mode at 1607 and 2227 cm⁻¹ are shown in Fig. 13. In contrast to those in step-scan mode where synchronization between perturbation and spectral acquisition is required, the reconstructed rapid-scanning spectral intensities show a nonmeaningful waveform. By shifting the time domain (3.9 ms in this case), one can make the spectral intensities show exactly the dynamic behavior observed by the stepscan technique (Figs. 13C and 13D). The obvious advantage of the new technique is the significantly shorter measurement time (2 min in rapid-scan mode vs. 1 h in stepscan mode).

CONCLUSION

A technique using rapid-scan FT-IR spectroscopy for observation of the dynamic changes of reversible phenomena has been introduced. By taking advantage of the periodic characteristics of the system, a carefully designed sampling rate with respect to the perturbation period, and reconstruction of observed spectral intensities, this approach allows one to obtain dynamic changes of the system within a single perturbation period. The reconstructed spectra from the rapid-scan technique show exactly the same dynamic behavior as those obtained by the step-scan technique. Although the rapid-scan technique cannot be applied to a system with rapid changes, it has some other advantages; for example, neither lockin amplifier nor synchronization between the perturbation and spectral acquisition is required. Furthermore, a short experimental time is achieved.

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