Field-effect transistor configuration for the measurement of infrared Stark spectra

Kenji Suzuki, Kenji Takashima, Yukio Furukawa*

Department of Chemistry, School of Science and Engineering, Waseda University, Shinjuku-ku, Tokyo 169-8555, Japan

Received 27 December 2005; received in revised form 28 April 2006; accepted 8 May 2006

Abstract

The infrared Stark spectrum of a thin film of poly(γ-benzyl-L-glutamate) (PBLG) has been measured in a field-effect transistor (FET) configuration, instead of the standard Stark cell with semitransparent metal electrodes. In the FET-type cell the PBLG film is sandwiched with an interdigital gold film and a SiO$_2$/n-Si substrate; the gold and n-Si have been used as electrodes. The obtained Stark spectrum is in good agreement with that in the literature. Each of the observed Stark bands, which are assigned to the NH str, the C=O str of the ester group, and the amide I, has been decomposed into the zeroth-, first-, and second-derivative components by the least-squares method. The effective electric field in the PBLG film has been estimated from the obtained second-derivative component for each vibrational mode on the basis of the reported difference electric dipole moment, following excitation to a vibrationally excited state. The effective electric field is 0.42 times as large as that of the corresponding capacitor with a plate electrode instead of the interdigital one. The FET-type cell can be used for the measurements of infrared Stark spectra on the basis of the obtained effective electric field.

Keywords: Vibrational Stark effect; Infrared spectroscopy; Poly(γ-benzyl-L-glutamate)

1. Introduction

When an electric field is applied across a molecule, both the vibrational levels and the transition dipole moment between the levels change slightly. These changes affect the infrared spectrum of the sample. Those are called the vibrational Stark effect (abbreviated as VSE) [1]. VSE gives us information on the physics of molecular vibrations such as the perturbation of chemical bonds by electric fields, anharmonicity of chemical bonds, etc. VSEs can provide a local probe of electric fields in various systems such as organic electronic devices, proteins, etc. An infrared Stark spectrum $\Delta A(\tilde{v})$ is the absorbance in the presence of an external electric field minus that without the field. From the observed infrared Stark spectrum, two molecular vibrational properties have been derived: the change in electric dipole moment $\Delta \mu$ and that in polarizability $\Delta \alpha$ between the initial and final vibrational states. The quantity $\Delta \mu$ is a measure of the amount of charge transfer associated with the transition; $\Delta \alpha$ is a measure of the sensitivity of the transition to an applied field and reflects on the vibrational properties of molecules interacting with an environment.

Although infrared Stark spectra have been reported for small molecules [2–5], proteins [6], and polypeptide [7,8], the number of samples measured is limited. It results from the difficulty in the measurements of infrared Stark spectra. It is troublesome to make semitransparent metal films that are used as the electrodes of a standard Stark cell. Imperfect semitransparent electrodes distort the shapes of infrared bands, which is crucial in infrared Stark spectra. Tsuji and Furukawa [9] have found the infrared Stark effect simultaneously when they have observed the gate-voltage-induced infrared absorption from an organic field-effect transistor (FET). However, the electric field in the organic layer in the FET configuration is not obvious. The use of the FET-type cell for the measurements of infrared Stark spectra requires the determination of the electric field in the sample layer. In this paper, we describe an FET-type cell for measuring the infrared Stark spectra of a polymer film. We obtain the effective electric field in a thin film of poly(γ-benzyl-L-glutamate) (PBLG, Fig. 1) in the FET configuration.
Infrared spectra were measured on a Varian FTS-7000e FT-IR spectrometer equipped with a linearized HgCdTe detector at room temperature. Infrared Stark spectra were measured in a transmission–absorption configuration by infrared difference spectroscopy [8,10]. Infrared light from the spectrometer was focused on the active area of the Stark cell with a 4 x beam condenser (Specac Model 02560). The diameter of the infrared beam on the cell was about 1.5 mm. Infrared light passed through the sample region between the fingers of the interdigital electrode. The drive of a dc voltage source (ADVANTEST R6161) was synchronized with the accumulation of the FT-IR spectrometer. The wavenumber resolution was 4 cm⁻¹. The measured spectra were interpolated so that the data interval was 0.24 cm⁻¹. In the difference-spectrum measurement, the interferograms from the device at the voltage of $V$ (V) was accumulated for 50 times, and then that at the voltage of 0 V was accumulated for 50 times. These procedures were repeated for 40 times. The total accumulation times are typically 2000 times for each voltage. The obtained intensity spectra were calculated in a usual way by the computer of the spectrophotometer. The calculated spectrum means the difference absorbance between the voltages of $V$ and 0 V.

3. Theory

An external electric field $\mathbf{F}$ yields a slight shift $\Delta \nu$ for each molecule in a sample. The change in transition energy due to an external applied field is given by [4]

$$hc \Delta \nu = -\Delta \mu(f \mathbf{F}) - \frac{1}{2} (f \mathbf{F}) \Delta \alpha(f \mathbf{F}),$$

(1)

where $h$ is the Planck’s constant, $c$ is the speed of light, $f$ represents a local field correction factor. Since the electric field at the molecule is greater than the applied field, the local field is expressed by $\mathbf{F}$. The first and the second terms are known as the linear and the quadratic Stark effect, respectively. The applied field also affects the transition dipole moment $\mathbf{M}(\mathbf{F})$ through the transition polarizability $\mathbf{A}$ and the transition hyperpolarizability $\mathbf{B}$:

$$\mathbf{M}(\mathbf{F}) = \mathbf{M} + A(f \mathbf{F}) + (f \mathbf{F}) \mathbf{B}(f \mathbf{F}).$$

(2)

Since in the solid samples and frozen glasses the orientational motion of a molecule is hindered, only the electronic polarization signals can be extracted. On the basis of Eqs. (1) and (2), the change in absorbance under the influence of an external field for an isotropic, immobilized sample can be quantitatively expressed as [1,4,5,11]

$$\Delta A(\tilde{\nu}) = (f \mathbf{F})^2 \left\{ A_z A(\tilde{\nu}) + \frac{B_z}{15hc} \frac{d}{d\tilde{\nu}} \left( \frac{A(\tilde{\nu})}{\tilde{\nu}} \right) \right\} + \frac{C_z}{30hc^2 \tilde{\nu}^2} \frac{d^2}{d\tilde{\nu}^2} \left( \frac{A(\tilde{\nu})}{\tilde{\nu}} \right).$$

(3)
with
\[
A_{\chi} = \frac{1}{30|M|^2} \sum_{i,j} \left[ 10A_{ii}^2 + (3 \cos^2 \chi - 1) \left( 3A_{ii} A_{jj} + A_{ij}^2 \right) \right] \\
+ \frac{1}{15|M|^2} \sum_{i,j} \left[ 10M_i B_{ij} + (3 \cos^2 \chi - 1) \left( 4M_i B_{ij} \right) \right],
\]
(4)

\[
B_{\chi} = \frac{5}{2} \text{Tr}(\Delta \mathbf{z}) + \left( 3 \cos^2 \chi - 1 \right) \frac{3}{2} \frac{M^2}{|M|^2} \text{Tr}(\Delta \mathbf{z}) - \frac{1}{2} \text{Tr}(\Delta \mathbf{z}) \\
+ \frac{1}{|M|^2} \left[ 10M_i A_{ij} \Delta \mu_j + (3 \cos^2 \chi - 1) \right] \\
\times \left( 3M_i A_{ij} \Delta \mu_i + M_i A_{ij} \Delta \mu_j \right),
\]
(5)

and
\[
C_{\chi} = \left| \Delta \mu \right|^2 \left[ 5 + (3 \cos^2 \chi - 1) (3 \cos^2 \zeta - 1) \right],
\]
(6)

where \( \chi \) is the angle between \( \mathbf{F} \) and the electric field vector of the polarized infrared light, and \( \zeta \) is the angle between \( \mathbf{M} \) and \( \Delta \mathbf{\mu} \). The coefficients \( A_{\chi}, B_{\chi}, \) and \( C_{\chi} \) are associated with molecular properties of the system.

In the present experiments \( \chi = 90^\circ \). It is assumed that the NH stretch, the C=O stretch, and the amide I behave as a one-dimensional oscillator, because this assumption is applicable to the CN stretch of several nitriles in a previous paper [4]. Thus, \( \mathbf{M} \) is parallel to \( \Delta \mathbf{\mu} \), i.e., \( \zeta = 0^\circ \). Therefore, one can derive the following equation from Eq. (6):
\[
C_{\chi} = 3 |\Delta \mu|^2.
\]
(7)

Thus, the absorbance originating from the second-derivative spectrum \( \Delta A^C(\tilde{\nu}) \) can be expressed as
\[
\Delta A^C(\tilde{\nu}) = (f \mathbf{F})^2 \frac{|\Delta \mu|^2}{10 \hbar^2 c^2} \frac{d^2}{d\tilde{\nu}^2} \left( A(\tilde{\nu}) \right).
\]
(8)

Eq. (8) shows the relation between \((f \mathbf{F})^2, |\Delta \mu|, \) and \( \Delta A^C(\tilde{\nu}) \).

4. Results and discussion

4.1. Stark spectrum

The infrared spectra of a PBLG cell are shown in Fig. 3a. The bands are observed at 3285, 1735, and 1653 cm\(^{-1}\), which can be assigned to the NH stretch, the C=O stretch of the ester group, and the amide I, respectively [12]. The infrared Stark spectra of a PBLG film with a voltage of 150 V are shown as black lines in Fig. 3b. Each Stark spectrum obtained in the FET configuration agrees well with that obtained in a cell with semitransparent metal electrodes [7,8]. Therefore, the FET can be used as a Stark cell.

Each band of PBLG has been fitted by a Voigt band shape. Each of the observed Stark bands has been decomposed into the original spectrum and its first- and second-derivative spectra derived from the Voigt bands by the least-squares fitting. The obtained zeroth-, first-, and second-derivative spectra are shown as yellow, blue, and

![Fig. 3.](https://example.com/fig3.png)

(a) Infrared spectrum of an FET-type cell with a PBLG film (black) and the fitted Voigt band (red), (b) the observed infrared Stark spectrum (black), and (c) the decomposed zeroth- (yellow), first- (blue), and second (green)-derivative components and the sum of them (red). The sum spectrum is also shown in (b) as a red line.
green lines, respectively, with the sum (red) of them in Fig. 3c. As is shown in Fig. 3b, each simulated sum spectrum (red) is in good agreement with the observed (black). Fig. 4a shows the amplitudes of the observed Stark signals as a function of the square of the applied electric field for the NH stretch, the C=O stretch, and amide I, demonstrating the expected quadratic dependence. This result also supports the usefulness of the FET cell for the measurement of infrared Stark effect. Fig. 4b shows the coefficients of the decomposed second-derivative spectrum as a function of the applied electric field. This coefficient is proportional to the square of the applied field. The second-derivative spectrum is associated with $|\Delta \mu|$ and $(f(F))^2$ as shown in Eq. (8); $|\Delta \mu|$ or $(f(F))^2$ can be determined form the experimental results.

### 4.2. Electric field in an FET configuration

One can determine the electric field for each applied voltage from the reported values of $|\Delta \mu|$ and the observed Stark spectra by using Eq. (8). Nakabayashi and Ohta [7] have reported that the values of $|\Delta \mu|$ for the NH stretch, the C=O stretch, and amide I are 0.11, 0.06, and 0.05 $D/f$, respectively. One of the present author Suzuki [8] has reported that the values of $|\Delta \mu|$ for these modes are 0.12, 0.048, and 0.040 $D/f$. Although the electric field is not uniform in the PBLG layer between the fingers of the interdigital electrode in the FET-type cell, it is assumed that the electric field in the PBLG layer is uniform as a crude approximation. Thus, the effective electric field $F_{\text{eff}}$ can be derived from the reported values of $|\Delta \mu|$ by using Eq. (8). We have calculated the values of $F_{\text{eff}}$ from the average values of $|\Delta \mu|$ reported previously [7,8]. The obtained electric fields are listed in the fourth column of Table 1.

We will correlate the obtained effective field with the voltage applied to the Stark cell. Consider a capacitor shown in Fig. 5a. In this capacitor the PBLG and SiO$_2$ layers are sandwiched with two electrodes, whereas the upper electrode of the Stark cell is an interdigital electrode as schematically shown in Fig. 5b. The thicknesses of the PBLG and the SiO$_2$ layers are $d_1$ and $d_2$, respectively. The relative dielectric constants of PBLG and SiO$_2$ are $\varepsilon_{r,1}$ and $\varepsilon_{r,2}$, respectively. When a voltage of $V$ (V) is applied between the electrodes, the electric field in the PBLG layer

| Voltage (V) | $F_C$ (MV cm$^{-1}$) | Mode       | $F_{\text{eff}}$ (MV cm$^{-1}$) | $F_{\text{eff}}/F_C$ |
|------------|----------------------|------------|-------------------------------|---------------------|
| 50         | 0.73                 | NH stretch | 0.36                          | 0.49                |
|            |                      | C=O stretch| 0.33                          | 0.45                |
|            |                      | Amide I    | 0.27                          | 0.38                |
| 70         | 1.02                 | NH stretch | 0.42                          | 0.41                |
|            |                      | C=O stretch| 0.49                          | 0.48                |
|            |                      | Amide I    | 0.42                          | 0.41                |
| 100        | 1.46                 | NH stretch | 0.63                          | 0.43                |
|            |                      | C=O stretch| 0.61                          | 0.42                |
|            |                      | Amide I    | 0.56                          | 0.38                |
| 150        | 2.18                 | NH stretch | 0.82                          | 0.38                |
|            |                      | C=O stretch| 0.88                          | 0.40                |
|            |                      | Amide I    | 0.77                          | 0.35                |

Average $0.42 \pm 0.01$

Fig. 5. Schematic device structures of (a) the capacitor consisting of PBLG and SiO$_2$ layers and (b) the Stark cell with an interdigital electrode.
$F_C$ can be expressed as

$$F_C = V \frac{\varepsilon_{r,2}}{d_1 \varepsilon_{r,1} + d_2 \varepsilon_{r,1}}. \quad (9)$$

Since $d_1 = 200 \, \text{nm}$, $d_2 = 500 \, \text{nm}$, $\varepsilon_{r,1} = 3.8$, and $\varepsilon_{r,2} = 3.9$ [13], $F_C$ has been obtained to be $1.46 \times 10^4 \, \text{V/cm}$. The electric field thus obtained for several applied voltages are shown in the second column of Table 1. The values of $F_{\text{eff}}/F_C$ are shown in the fifth column. The average value has been obtained to be $0.42 \pm 0.01$. When we will study the infrared Stark effect of a sample using the FET-type cell, we can calculate the electric field in the sample layer of the cell by using this value.

5. Conclusions

The infrared Stark spectra of a thin film of PBLG have been measured by using an FET-type cell with the Au/PBLG/SiO$_2$/n-Si structure. In this cell, the interdigital gold and n-Si electrodes have been used instead of semitransparent metal electrodes in the standard Stark cell. Each of observed Stark bands has been decomposed into the zeroth-, first-, and second-derivative components. By using the electric dipole moment difference between the ground and the first excited vibrational levels in the literature and the obtained second-derivative spectra, the effective electric field in the PBLG layer has been derived. The effective field is 0.42 times as large as that of the corresponding capacitor. We have demonstrated that the FET-type cell can be used for the measurements of infrared Stark spectra. This method will be a useful probe of the electric field in an organic semiconductor layer of electronic devices.

Acknowledgments

This work was supported in part by the Grant-in-Aid for Scientific Research (A) (No. 16205004) from JSPS and the 21COE ‘Practical Nano-Chemistry’ from MEXT.

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