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Electroabsorption Spectroscopy of 6-Hydroxyquinoline Doped in Polymer Films: Stark Shifts and Orientational Effects

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Stark absorption spectroscopy was applied to 6-hydroxyquinoline (6-HQ) doped in polymer films of poly(methyl methacrylate) (PMMA) and poly(vinyl alcohol) (PVA) at temperatures of 50–300 K. The electroabsorption (E-A) spectrum of 6-HQ markedly depends on temperature in a PMMA film. The polarization dependence as well as the temperature dependence of the E-A spectra reveals that 6-HQ is oriented along the direction of the applied electric field at room temperature in a PMMA film. As the temperature becomes lower, the field-induced orientation of 6-HQ is restricted, and only the Stark shift induced by a change in electric dipole moment and in molecular polarizability is observed. On the other hand, E-A spectra of 6-HQ doped in a PVA film are essentially independent of temperature, suggesting that 6-HQ is not oriented along the electric field even at room temperature in PVA. These results show that the molecular motion of 6-HQ in a polymer film is very sensitive to the microenvironment of the surrounding matrix.

1. Introduction

Stark absorption spectroscopy is one of the most reliable techniques for obtaining quantitative information on electrostatic properties such as electric dipole moment (μ), molecular polarizability (α) or their changes following photoexcitation.^{1–5} It is also a sensitive method for the study of molecular motion in the presence of electric field both in the gas phase and in the condensed phase.^{6–10} We had considered that large molecules such as benzene derivatives doped in a solid polymer film may be immobile below glass transition temperatures because of the small free volume.¹¹ However, polarization dependence as well as temperature dependence of the electroabsorption spectra have convinced us that quite large molecules can be oriented along the applied electric field even in a polymer film below glass transition temperatures; indole and methylindole were shown to be partially oriented along the applied electric field at room temperature in a poly(methyl methacrylate) (abbreviated as PMMA) film.^{8,12}

Photophysical and photochemical behaviors of quinoline derivatives in various media have attracted much attention not only from the fundamental points of view but also from the usefulness in various applications.^{13–25} In 6-hydroxyquinoline (6-HQ), for example, the electronic excitation to the S_1 state strongly modifies the acid–base properties of this molecule, making the hydroxyl group more acidic and the nitrogen more basic in the excited state. 6-HQ revealed a two-step proton-transfer process in solution,^{13,16} and recent findings suggest the possibility of excited-state multiple proton transfer from hydroxyl group to ring nitrogen through H-bonded network composed of methanol and water cluster.¹⁹ The charge-transfer process in 6-HQ has been also discussed in an ion-exchange polymer film,²⁰ and it was suggested that the hydrogen bonding plays a key role in charge transfer as well as in proton-transfer reaction.

It has been suggested that molecular polarizability makes a substantial contribution to the solvation response even in the case of polar molecules.²⁶ Although a number of works were devoted toward the photophysical studies of 6-HQ, however, not much attention has been paid toward the measurement of the magnitude of $\Delta\alpha$ as well as the magnitude of $\Delta\mu$ following photoexcitation, though these parameters are undoubtedly the key factors to describe the electronic structure of the chromophores in both the ground and excited electronic states.

In the present study, the difference in electric dipole moment ($\Delta\mu$) and the difference in polarizability ($\Delta\alpha$) between the ground and first excited electronic states of 6-HQ doped in a PMMA film and in a poly(vinyl alcohol) (PVA) film were obtained, on the basis of the measurements of the electroabsorption spectra, i.e., E-A spectra. The E-A spectra were measured at different temperatures and at different angles between the applied field direction and the polarization direction of the excitation light. The results were analyzed to determine the change in electrostatic properties following photoexcitation and to figure out the field induced molecular orientation.

2. Experimental Section

6-HQ (Aldrich) was purified by a recrystallization from ethanol. PMMA (Aldrich, MW = 120 000) and PVA (Aldrich, MW = 146 000–186 000) were purified by a precipitation in a mixture of benzene and methanol and in a mixture of water and methanol, respectively. All the solvents were spectroscopic grade and used without further purification. Ultrahigh purified water was used in the experiment. PMMA and PVA films containing 6-HQ were prepared by a spin coating method on a nonemissive silica glass plate precoated with a conductive indium–tin oxide (ITO) layer. To avoid the aggregation of the sample chromophores, the concentration of the 6-HQ relative to the monomer unit of PMMA or PVA was chosen to be as low as 2 mol %. After the cast of the sample film, the film was dried in a vacuum oven at 50 °C for 24 h. The thickness of the polymer film of PMMA or PVA, which includes 6-HQ, which was measured with an interferometer microscope (Nanometrics,

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NanoSpec/AFT 010-0180), was typically 1.0 and 1.4 μm , respectively.

A semitransparent aluminum (Al) film was deposited on the 6-HQ-doped polymer films by a vacuum vapor deposition technique. Al and ITO films were used as electrodes for applying electric field. The strength of the applied electric field (40 Hz) was estimated from the applied ac voltage divided by the thickness of the sample films.

Absorption measurements were performed with a Hitachi U-3500 spectrophotometer. For the electroabsorption measurements, the converging light beam from JASCO FP-777 spectrofluorometer was collimated with a pinhole having a diameter of 1.4 mm and with a lens having a focal length of 20 mm and directed through a 10 mm aperture α -barium borate (BBO) polarization prism and through the sample slide on an external photomultiplier.⁸ A rotatory stage was used for varying the angle between the polarization direction of the excitation light and the direction of the applied field. A signal from the photomultiplier was amplified and divided into two channels. The dc component of the transmitted light intensity was recorded in a computer, and the ac component synchronized with the applied voltage was detected by a lock-in amplifier (SRS, SR830) at the second harmonic of the modulation frequency of the applied electric field. The amplitude and the phase signal from the output of the lock-in amplifier, which give the field induced change in transmitted light intensity, $\Delta I(2\nu)$, were digitized and recorded in the computer together with the dc component. Polarization measurements of the E-A spectra were carried out in air. The E-A spectra of 6-HQ were obtained at normal incidence ($\chi = 90^\circ$) and magic angle ($\chi = 54.7^\circ$), where χ is the angle between the direction of the applied electric field and the electric vector of the excitation light. Note that the field-induced change in absorption intensity is defined as $\Delta A = -(2\sqrt{2}/\ln 10)\Delta I(2\nu)/I$, where the factor $2\sqrt{2}$ converts the value of measured rms signal to its value.

Temperature dependence of the E-A spectra was examined with a nonpolarized absorption light crossing the sample slide at normal incidence in the range of 50–300 K in vacuo.²⁷ The sample substrate was cooled using a cryogenic refrigerating system (Daikin, V202C5LR) equipped with quartz optical windows, and the temperature of the substrate was controlled and monitored using a temperature controller (Scientific Instruments, model 9600) having a silicon diode thermometer (Scientific Instruments, Si-410A).

3. Theoretical Background of E–A Spectra

Electric field effects on absorption spectra as well as on emission spectra were described,^{5,28,29} on the basis of the theory developed by Liptay.⁴ Energy levels of a molecule or molecular system are influenced by an electric field, depending on the magnitude of μ and α in the states under consideration. As a result, optical spectra show a shift or/and a broadening. The change in transition energy (ΔE) is given by

$$\Delta E = -\Delta\mu \cdot \mathbf{F} - \frac{1}{2}\mathbf{F} \cdot \Delta\alpha \cdot \mathbf{F} \quad (1)$$

where $\Delta\mu$ and $\Delta\alpha$ are the differences in dipole moment vector and molecular polarizability tensor, respectively, between the ground and excited states, and \mathbf{F} is an applied electric field.

With the assumption of an isotropic distribution of the molecules in PMMA and PVA polymer films, the change in absorption intensity (ΔA) as function of wavenumber, ν , in the presence of \mathbf{F} , can be expressed as the sum of the zeroth, first and second derivatives of the absorption spectrum as follows:^{4,5,28,30}

$$\Delta A(\nu) = (fF)^2 \left[A_\chi A(\nu) + B_\chi \nu \frac{d}{d\nu} \left\{ \frac{A(\nu)}{\nu} \right\} + C_\chi \nu \frac{d^2}{d\nu^2} \left\{ \frac{A(\nu)}{\nu} \right\} \right] \quad (2)$$

where f is the internal field factor, and $F = |\mathbf{F}|$. As will be mentioned later, the absorption intensity of 6-HQ is not influenced by an electric field at low temperatures irrespective of polymer matrix, indicating that the field-induced change in absorption intensity of 6-HQ is negligible as far as molecules are fixed in vacuo. By neglecting the field-induced change in transition moment polarizability and hyperpolarizability, one can express the coefficients A_χ , B_χ , and C_χ as follows:

$$A_\chi = \frac{\mu^2}{30k^2T^2} (3 \cos^2 \chi - 1)(3 \cos^2 \xi - 1) + \frac{1}{10kT} (3 \cos^2 \chi - 1)(\alpha_m - \bar{\alpha}) \quad (3)$$

$$B_\chi = \frac{\Delta\bar{\alpha}}{2hc} + \left\{ \frac{(\Delta\alpha_m - \Delta\bar{\alpha})(3 \cos^2 \chi - 1)}{10hc} \right\} + \frac{\mu\Delta\mu}{3hckT} \cos \gamma + \left(\frac{\mu\Delta\mu}{15hckT} \right) (3 \cos^2 \chi - 1)(3 \cos \eta \cos \xi - \cos \gamma) \quad (4)$$

$$C_\chi = (\Delta\mu)^2 \left\{ \frac{5 + (3 \cos^2 \chi - 1)(3 \cos^2 \eta - 1)}{30h^2c^2} \right\} \quad (5)$$

where c is the speed of light, k is the Boltzmann constant, T is temperature, and μ is the magnitude of the ground-state dipole moment, μ_g . $\Delta\alpha_m$ and α_m represent the diagonal component of $\Delta\alpha$ and the polarizability in the ground state, α_g , with respect to the direction of the transition moment, respectively. The factors $\Delta\mu$ and $\Delta\bar{\alpha}$ are given by the following equations

$$\Delta\mu = |\Delta\mu| \quad \text{and} \quad \Delta\bar{\alpha} = \frac{1}{3}\text{Tr}(\Delta\alpha) \quad (6)$$

η is the angle between the direction of $\Delta\mu$ and the transition dipole moment. The value of η is useful because it may describe the direction of charge separation in the molecular axis systems associated with the transition. ξ is the angle between μ_g and the transition dipole moment, and γ is the angle between $\Delta\mu$ and μ_g . Temperature-dependent terms in eqs 3 and 4 arise from the field-induced molecular orientation. If molecules are completely immobile in polymer films with a random distribution, these terms can be neglected because the isotropic distribution of the molecular dipoles corresponds to a very high temperature where molecules rotate freely and quickly. By examination of the temperature dependence, therefore, molecular motion in the presence of electric field may be well understood. If the magnitude of $\Delta\mu$ following optical absorption is significant, the presence of \mathbf{F} will broaden an isolated transition, giving rise to the E-A spectrum, the shape of which is the second derivative of the absorption spectrum. If the magnitude of $\Delta\bar{\alpha}$ is significant, the shape of the E-A spectrum is the first derivative of the absorption spectrum. By evaluating the temperature-independent terms of the first and second derivatives in eqs 4 and 5, respectively, therefore, one can determine the magnitudes of $\Delta\bar{\alpha}$ and $\Delta\mu$.

4. Results

Polarized E-A spectra of 6-HQ doped in a polymer film were measured at room temperature under the atmospheric conditions.

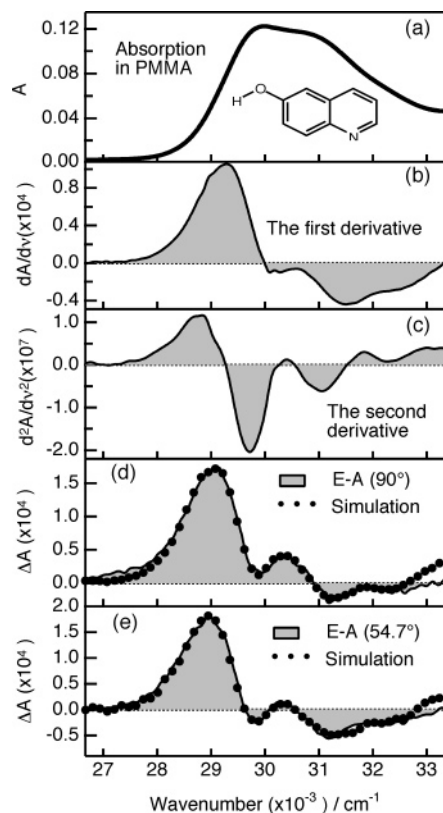


Figure 1. (a) Absorption spectrum of 6-HQ doped in a PMMA polymer film at a concentration of 2 mol % at room temperature, (b) and (c) the first and second derivative spectra of the above absorption spectrum, respectively, (d) E-A spectrum observed at room temperature with $\chi = 90^\circ$ and the simulated spectrum, and (e) E-A spectrum observed at room temperature with $\chi = 54.7^\circ$, and the simulated spectrum. See the text for the simulation. The applied electric field strength was 0.7 MV cm^{-1} .

Figure 1 shows the absorption spectrum, its first and second derivative spectra and E-A spectra of 6-HQ doped in a PMMA film at 2 mol % observed with the normal incident light, i.e., $\chi = 90^\circ$ for transition to the lowest electronically excited singlet state in the region from 300 to 375 nm, i.e., $\sim 26\,700$ to $\sim 33\,300 \text{ cm}^{-1}$.

The E-A spectrum observed with the magic angle of $\chi (= 54.7^\circ)$ is also shown in Figure 1. These E-A spectra were measured with the applied field strength of 0.7 MV cm^{-1} . Similar experiments were carried out for 6-HQ doped in a PVA film at room temperature. The results are shown in Figure 2. The spectral shape and the band maximum of the absorption spectra, which are nearly the same in both polymers, are similar to those of the solution spectra observed in polar and nonpolar solvents.¹⁹ As shown in Figures 1 and 2, the absorption spectra show a band maximum at around 333 nm ($\sim 30\,000 \text{ cm}^{-1}$) and 332 nm ($\sim 30\,120 \text{ cm}^{-1}$), respectively, in PMMA and PVA films. It is worth mentioning that E-A spectra in the normal-incident case and in the magic angle case for χ are different from each other especially for 6-HQ doped in PMMA (cf. E-A spectra in Figure 1d,e at around $30\,000 \text{ cm}^{-1}$). In contrast with the E-A spectra in PMMA, E-A spectra in the normal-incident case and in the magic angle case for χ show essentially the same shape in a PVA film, as shown in Figure 2.

E-A spectra of 6-HQ doped in PMMA were simulated by a linear combination of the zeroth, first, and second derivatives of the absorption spectrum, as expected from eq 2. The simulated spectra are shown in Figure 1, together with the observed spectra. From the simulation, the coefficients of the

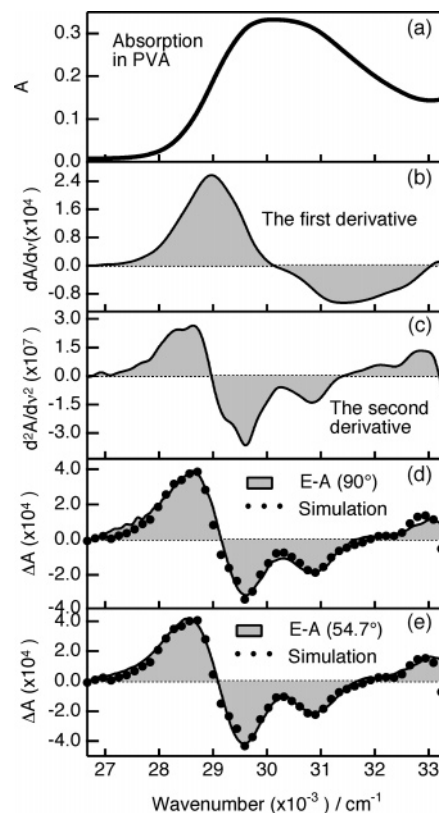


Figure 2. (a) Absorption spectrum of 6-HQ doped in a PVA polymer film at a concentration of 2 mol % at room temperature, (b) and (c) the first and second derivative spectra of the above absorption spectrum, respectively, (d) E-A spectrum observed at room temperature with $\chi = 90^\circ$ and the simulated spectrum, and (e) E-A spectrum observed at room temperature with $\chi = 54.7^\circ$, and the simulated spectrum. See the text for the simulation. The applied electric field strength was 0.7 MV cm^{-1} .

TABLE 1: Coefficients Used To Simulate the E-A Spectra of 6-HQ Doped in PMMA Films

	<i>T</i> /K	χ /deg	$A_\chi/\text{cm}^2 \text{ MV}^{-2}$	$B_\chi/\text{cm} \text{ MV}^{-2}$	C_χ/MV^{-2}
in air	295	90	8.2×10^{-4}	2.7	6.5×10^2
		54.7	3.1×10^{-4}	2.7	7.6×10^2
in vacuo	57 ^a	90	0	0.3	8.7×10^2
	295	90	2.0×10^{-4}	1.6	5.4×10^2

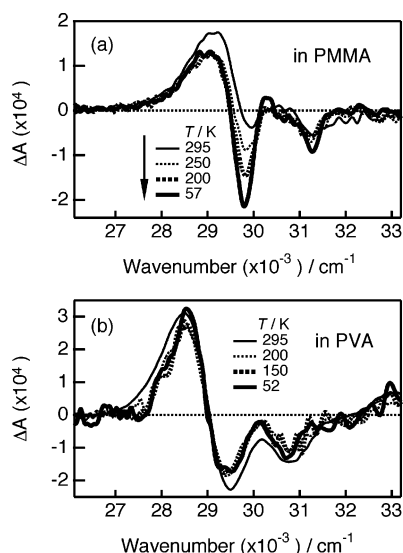
^a Uncertainty in temperature is $\pm 4 \text{ K}$.

zeroth, first, and second derivatives, i.e., A_χ , B_χ , and C_χ in eq 2 were determined with the normal incident light in a PMMA film, as shown in Table 1. In the magic angle case, E-A spectra in PMMA were similarly simulated (see Table 1). It is noted that the magnitude of ΔA is proportional to the square of the applied electric field. It is worth mentioning that the zeroth component is much larger in the normal incident case of χ than in the magic angle case, implying that the field-induced orientational effect cannot be neglected.

E-A spectra of 6-HQ doped in a PVA film measured both at normal incident angle and at magic angle could be well simulated by a linear combination of the first and second derivative components of the absorption spectrum, and the zeroth derivative component of the absorption spectrum was unnecessary to be considered. From the simulation of the observed E-A spectra, the coefficients of the first and second derivatives in PVA were determined both at the magic angle of χ and at the normal incident, as shown in Table 2. The fact that the first derivative component is larger at $\chi = 90^\circ$ than that at $\chi = 54.7^\circ$ implies that the second or fourth term of eq 4 is not negligible.

TABLE 2: Coefficients Used To Simulate the E-A Spectra of 6-HQ Doped in PVA Films

	T/K	χ/deg	$A_\chi/\text{cm}^2 \text{ MV}^{-2}$	$B_\chi/\text{cm} \text{ MV}^{-2}$	C_χ/MV^{-2}
in air	295	90	0	1.0	2.2×10^3
		54.7	0	0.7	2.1×10^3
in vacuo	52 ^a	90	0	1.0	2.2×10^3

^a Uncertainty in temperature is ± 4 K.**Figure 3.** Temperature dependence of the E-A spectra of 6-HQ doped in a PMMA film (a) and in a PVA film (b) observed with $\chi = 90^\circ$. The concentration of 6-HQ was 2.0 mol % in both cases, and the applied electric field strength was 1.0 and 0.7 MV cm⁻¹ for the PMMA and the PVA films, respectively.

E-A spectra of 6-HQ doped in PMMA and PVA films were also measured in a wide range of temperature (from 295 to 50 K) in vacuo, and the results are shown in Figure 3. In PVA, the E-A spectra of 6-HQ are nearly the same even when the temperature is varied from ~ 50 to 295 K except for a slight change in intensity and a slight narrowing of the spectral shape at lower temperatures, which probably come from the temperature dependence of the spectral shape of the absorption spectrum. In PMMA, on the other hand, E-A spectra markedly depend on the temperature, as shown in Figure 3a. As mentioned above, E-A spectra of 6-HQ doped in a PMMA film observed at room temperature are simulated by a linear combination of the zeroth, first and second derivatives of the absorption spectrum. At a low temperature of ~ 50 K, on the other hand, E-A spectrum of 6-HQ doped in PMMA could be simulated by a linear combination between the first and second derivatives of the absorption spectrum, and the zeroth derivative component was not necessary to be considered, as in the case of the E-A spectra in PVA. The result of the simulation for the E-A spectrum of 6-HQ in PMMA at 57 K is shown in Figure 4, and the coefficients of the first and second derivatives were determined (see Table 1). Note that the quadratic field strength dependence of ΔA was observed at any temperature. It is worth mentioning that E-A spectra of 6-HQ doped in PMMA observed at room temperature in vacuo are slightly different from the ones observed under the atmospheric conditions at room temperature (cf. Figures 1d and 3a/4d). The simulation was also done for the E-A spectrum in PMMA observed in vacuo at room temperature. The results are shown in Figure 4, and the coefficients of the zeroth, first and second derivatives used in the simulation are shown in Table 1. It is worth mentioning that the zeroth derivative component at room temperature in vacuo is smaller than that under the atmospheric conditions.

To examine the temperature dependence of the E-A spectra in PMMA, plots of the difference between ΔA_R and ΔA_T observed at 335 nm ($\sim 29\,850 \text{ cm}^{-1}$) were obtained as a function of temperature. Here, ΔA_R and ΔA_T are the field-induced change in absorption intensity at room temperature and at a temperature of T , respectively. The results are shown in Figure 5a. Note that a remarkable temperature dependence of ΔA was observed at 335 nm (see Figure 3a). As the temperature decreases, the magnitude of ΔA_T at 335 nm gradually decreases and reaches a constant value at around 100 K. Even when the temperature is further lowered from ~ 100 to 57 K, the variation in intensity is very small.

5. Discussion

When the molecules doped in a polymer film have a large dipole moment in the ground state, the molecules will have a tendency to orient along the electric field applied in the Stark experiment, unless the polymer matrix is sufficiently rigid to prevent its motion. Complete reorientation of the molecules is unlikely in a polymer film, but rotations of smaller angles may still occur in a polymer matrix. In fact, field-induced orientation of coumarine molecules doped in a polymer film were reported not only in polymers above the glass transition temperatures but also in polymers below their glass transition temperatures under some circumstances.⁷ Through the polarization measurements of the E-A spectra, smaller dipolar orientation at room temperature, which is much lower than the glass transition temperature of the polymer matrix, was also found for indole doped in a PMMA film in the presence of the external electric field, though the angular mobility of indole is restricted by the PMMA host matrix.⁸

The terms that contain the Boltzmann factor, i.e., $1/(kT)$, in eqs 3–5 correspond to the field-induced molecular orientation, and so the temperature dependence of the E-A spectra is extremely useful to confirm the field-induced orientation. When dopant molecules of 6-HQ are randomly distributed in a rigid polymer film and cannot reorient in the presence of electric fields, these terms can be neglected. As a result, the magnitude of $\Delta\mu$ and/or $\Delta\alpha$ may be easily evaluated from the E-A spectra without consideration of the orientational effect. As mentioned above, E-A spectra of 6-HQ doped in a PVA film are essentially independent of the temperature, suggesting that 6-HQ is fixed in a PVA film. It is considered that molecular dipoles of 6-HQ remain random in PVA and that the dopant molecules of 6-HQ are not oriented along the field direction at temperatures lower than 300 K even with the electric fields as strong as $\sim 1 \text{ MVcm}^{-1}$. The fact that the zeroth derivative component is negligible in PVA at both angles of 90° and 54.7° for χ seems to support that the field-induced orientation has been restricted in PVA. Note that the first term A_χ in eq 2, defined by the zeroth-derivative of the absorption spectrum, is ascribed to the change in absorption intensity arising from the deviation of the transition dipole from the isotropic distribution by the alignment and orientation of the molecules along the field direction.

The immobility of 6-HQ in PVA can be attributed to the small size of the cavity of PVA where 6-HQ is embedded and/or the large interaction between 6-HQ and the surrounding PVA matrix. As far as the free volume/rigidity is concerned, PVA has a larger free volume and possibly less rigidity than PMMA.²⁰ Therefore, the possibility of faster equilibration or mobility of guest chromophores can be more expected in the cavity of PVA than in PMMA. The distance between the two functional groups in 6-HQ is 10 \AA ,¹⁵ which points toward the availability of the sufficient free volume in polymers. Then, it may be reasonably

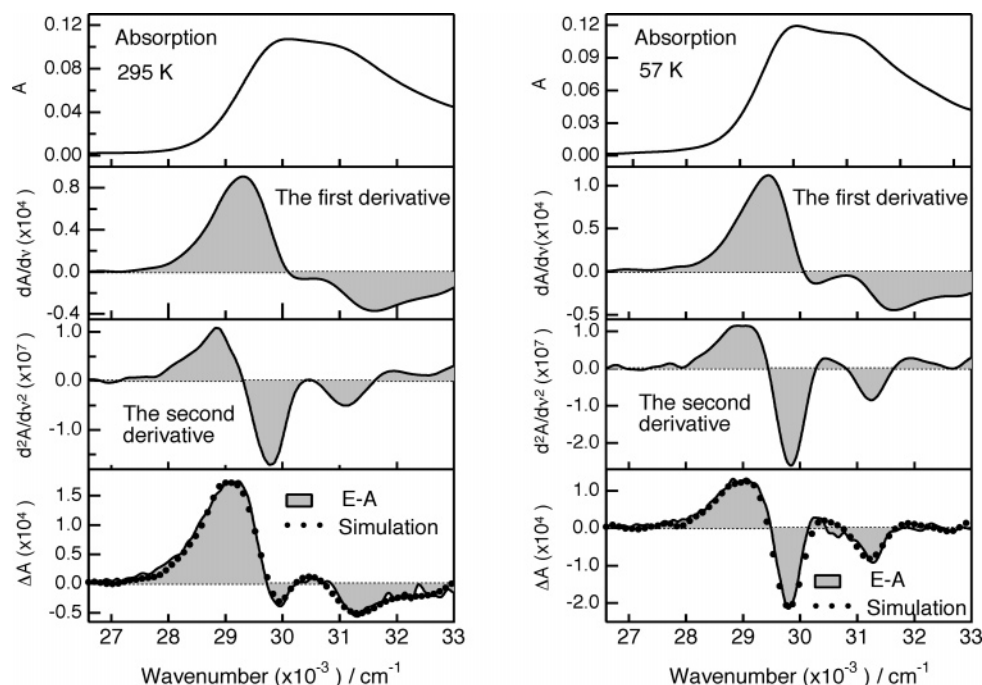


Figure 4. E-A spectra of 6-HQ doped in a PMMA film observed in vacuo with $\chi = 90^\circ$ at 295 and 57 K, respectively, and the simulated spectra, together with the absorption and its first and second derivative spectra. The applied field strength was 1.0 MV cm^{-1} . See the text for the simulation.

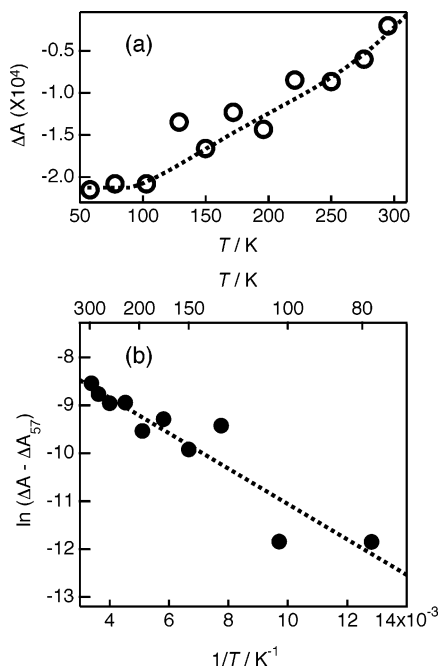


Figure 5. (a) Plots of ΔA observed at 335 nm for 6-HQ doped in a PMMA film as a function of temperature (T) and (b) plots of the difference of $\Delta A - \Delta A_{57}$, where ΔA_{57} is the field-induced change in absorption intensity at 57 K, in logarithmic scale as a function of T^{-1} . The dotted line in (a) is just a guide to trace the temperature dependence of the data, and the dotted line in (b) is a least-squares fitting to the data. The applied electric field strength was 1.0 MV cm^{-1} .

considered that 6-HQ is not oriented along the electric field because the interaction between 6-HQ and the surrounding PVA matrix is very strong, even when an electric field as large as $\sim 1 \text{ MV cm}^{-1}$ is applied. Note that the molecular orientation/alignment occurs when the rotational energy exceeds the interaction between 6-HQ and the matrix.

E-A spectra of 6-HQ in PVA are very similar in shape to the second derivatives of the absorption spectra (see Figure 2),

TABLE 3: Magnitude of $\Delta\mu$ and $\Delta\bar{\alpha}$ Obtained from the E-A Spectra of 6-HQ Doped in Polymer Films^a

polymer	$\Delta\mu/D$	$\Delta\bar{\alpha}/\text{\AA}^3$
PVA	6.8 ± 1.0	26 ± 8
PMMA	4.3 ± 0.6	11 ± 4

^a The reported values are not corrected for the internal field factor.

which suggests that the Stark shift induced by a change in electric dipole moment following absorption is the dominant electric field effect. Actually, the first derivative component of the absorption spectrum is necessary to reproduce the observed E-A spectra, as mentioned already, implying that $\Delta\bar{\alpha}$ is not zero. From the contribution of the first and second derivative components in the E-A spectra observed with $\chi = 54.7^\circ$, the magnitudes of $\Delta\mu$ and $\Delta\bar{\alpha}$ were determined. The results are shown in Table 3. Note that the terms other than the first term become zero in eqs 4 and 5 with $\chi = 54.7^\circ$, when E-A spectra are independent of the temperature. As mentioned above, the first derivative component has a significant difference between the E-A spectra observed with $\chi = 90^\circ$ and 54.7° in PVA. As seen in eq 4, this difference can be attributed to the anisotropic property of the molecular polarizability; $\Delta\alpha_m \neq \Delta\bar{\alpha}$. When eq 5 was combined with the χ dependence of the second derivative component of the observed E-A spectra, the angle between the transition dipole moment and the change in dipole moment was evaluated to be 52° in PVA.

In contrast with the results in PVA, E-A spectra of 6-HQ doped in a PMMA film markedly depend on the temperature (see Figure 3a). The zeroth derivative component of the absorption spectrum is significant in the E-A spectra of 6-HQ doped in PMMA at room temperature, especially in the normal incident case, i.e., $\chi = 90^\circ$. As the temperature decreased from room temperature to $\sim 50 \text{ K}$, the shape of the E-A spectra changed gradually from the one similar to the first derivative to that similar to the second derivative of the absorption spectrum (see Figure 3). Below 100 K, the observed E-A spectra were very similar in shape to the second derivative of the absorption spectrum, and the contribution of the zeroth derivative compo-

nent vanishes, which indicates that the contribution of the orientational polarizability is minimized at temperatures below 100 K. Thus, the electric field effects on absorption spectra of 6-HQ doped in a PMMA film at room temperature can be explained in terms of the field-induced orientation/alignment of embedded polar molecules of 6-HQ in PMMA environment, though there is no doubt that the Stark shift is also induced. The much smaller first derivative component as well as the negligible zeroth component in the cryogenic E-A spectra is a direct consequence of the absence of orientational effects in PMMA at temperatures lower than 100 K. As the temperature decreases, the Stark shift resulting from $\Delta\mu$ following photo-excitation becomes dominant. It is noted that the first derivative component was also necessary to well simulate the E-A spectra at temperatures below 100 K, though its contribution was very small. At low temperatures below 100 K, 6-HQ is regarded as immobile and distributed randomly in PMMA; the temperature-dependent terms in eqs 3–5 can be neglected. The magnitude of $\Delta\mu$ was evaluated by comparing the second derivative component of the E-A spectra observed with $\chi = 90^\circ$ in PMMA at 57 K with the corresponding one of the E-A spectra observed with $\chi = 90^\circ$ in PVA at 52 K, by assuming that the angle between the direction of $\Delta\mu$ and the transition dipole moment, i.e., η in eq 5 is the same both in PMMA and in PVA. Then, $\Delta\mu$ in PMMA has been determined (see Table 3). The magnitude of $\Delta\alpha$ of 6-HQ doped in PMMA has been also determined, on the basis of the E-A spectra observed at 57 K, by assuming that the polarizability is isotropic. The results are shown in Table 3.

If the zeroth derivative component in eq 1 comes only from the field-induced orientational effect, its value must be zero in the magic angle case of χ ; A_χ of eq 2 is zero with $\chi = 54.7^\circ$. Under the atmospheric condition, however, the zeroth derivative component is not zero in PMMA at room temperature even in the magic angle case of χ , though the value in the magic angle case was much smaller than the one observed in the normal incident case for χ . In vacuo, on the other hand, the zeroth derivative component in PMMA is very small at room temperature even in the normal incident case of χ (see Table 1). These results suggest that the absorption intensity is a little enhanced by an electric field only under the atmospheric conditions. Unfortunately, the effect of air on the E-A spectra could not be examined at low temperatures because the low temperature experimental conditions could be obtained only in vacuo. Actually, the role of air remains unsettled, but it is inferred that air, i.e., probably oxygen induces a field-induced enhancement in transition moment of 6-HQ as a result of the strong interaction between 6-HQ and oxygen which may coexist in the cavity of PMMA. The absorption intensity may increase as a result of the field-induced borrowing of the intensity from higher charge-transfer bands between 6-HQ and oxygen. The difference of the zeroth derivative component between in vacuo and in air is nearly the same order of magnitude as the zeroth derivative component observed at the magic angle at room temperature. Then, it may be considered that the field-induced enhancement in transition moment which occurs under the atmospheric conditions disappears in vacuo.

As the temperature decreases, the translational energy as well as the rotational energy of molecules becomes smaller. In a polymer film, 6-HQ is considered to be confined to a cavity produced by PMMA or PVA, and then the molecular motion of 6-HQ is limited inside the cavity. If the cavity size, i.e., free volume of the polymer, is small enough, not only the translational motion but also the rotational motion will be prevented

in a cavity. The present results show that the size of the cavity where 6-HQ is embedded is not small enough in PMMA to prevent the rotational motion of 6-HQ. In contrast with the PVA matrix, further, the interaction between 6-HQ and the surrounding matrix of PMMA is not large enough to prevent the rotational motion in the cavity. We therefore expect that considerable mobility of the dopant molecule of 6-HQ is possible in PMMA at room temperature. On the other hand, the environment of 6-HQ is very rigid in PVA, and the dopant molecules are not mobile, though the room temperature is much lower than the glass-transition temperature (T_g) of both PMMA and PVA. Note that T_g of PMMA and PVA is 378 and 353 K, respectively.^{31,32}

As the temperature decreases, the rotational energy of 6-HQ relative to the interaction between 6-HQ and the PMMA matrix becomes smaller, and the field-induced orientation is hindered at temperatures below 100 K. By assuming that the internal energy of 6-HQ must exceed the potential barrier produced by the interaction between 6-HQ and the surrounding matrix of PMMA for the field-induced molecular orientation, one may give the temperature dependence by a Boltzmann factor; $\Delta(\Delta A)/A$ is proportional to $\exp(-\Delta E_v/kT)$, where ΔE_v is the barrier height that corresponds to the interaction between 6-HQ and PMMA matrix. From the plots of $\Delta(\Delta A)$ as a function of T^{-1} given in Figure 5b, ΔE_v is estimated to be ~ 260 cm⁻¹. The fact that the field-induced orientation does not occur at room temperature in PVA implies that the interaction between 6-HQ and PVA, i.e., the adsorption energy of 6-HQ on PVA, is extremely large. It is likely that this strong interaction causing the rigidity of 6-HQ is ascribed to the hydrogen-bonding formation between 6-HQ and PVA matrix. It may be said that not only PVA but also PMMA show hydrogen bonding with 6-HQ, and another possibility may be pointed out for the difference between PMMA and PVA. In a polymer having a side chain such as PMMA, a motion of the side chain may be different from the main-chain motion. Even below the glass transition temperatures, such a side chain may influence the microenvironments of the molecules doped in the polymer film. As a result, the presence of the side chain in PMMA may give the different temperature dependence from that in PVA.³³

Finally, the present results that the E-A spectra are fitted well with the derivatives of the observed absorption spectra in both polymers preclude the possibility of the multiple allowed electronic transitions. It seems that absorption band of 6-HQ consists of only single optically allowed transition both in PMMA and in PVA polymer films in the spectral region under the present study. Our preliminary results of the Hartree–Fock and density functional theory methods show that both cis- and trans-rotamers of 6-HQ (with opposite orientations of the O–H group relative to the quinoline frame) can be present with the energy difference between these rotamers that is rather small (~ 0.14 eV) and that the permanent dipole moment in the ground state is to be 1.3 and 3.0 D in cis and trans rotamers, respectively.³⁴ The two-color resonant two-photon ionization spectrum also provides the evidence of the rather small energy separation between cis and trans isomers, and it is reported that the vibronic origins of the $S_0 \rightarrow S_1$ transition of cis- and trans-rotamers are separated by only 297 cm⁻¹ in a supersonic jet.¹⁵ Both cis and trans rotamers show similar vibrational structures in the absorption spectrum with a small energy separation.¹⁵ Therefore, it is considered that the absorption spectra of cis and trans rotamers cannot be distinguished from each other with the present spectral resolution, even when both rotamers coexist in a polymer film. A shoulder located at ~ 1100 cm⁻¹ above

the strongest peak of the absorption spectrum of 6-HQ in PMMA is assigned as the vibrational structure; the band shape of the main absorption region, which is composite, is ascribed to the vibrational structure of the $S_0 \rightarrow S_1$ transition of 6-HQ irrespective of cis and trans rotamers. As mentioned above, the observed E-A spectra are well simulated by using the derivative components of the whole absorption spectrum both in PMMA and in PVA, indicating that all the vibronic bands show the same Stark shifts in both polymer films. If the absorption spectrum is composed of cis and trans rotamers, the E-A spectrum seems not to be reproduced by considering the derivative components of the whole spectrum. As expected from the calculation, the dipole moments of cis and trans rotamers are quite different from each other, and both rotamers should give different E-A spectra from each other. Therefore, the fact that the E-A spectra are reproduced with the derivative components of the whole absorption spectra without decomposing the absorption spectrum into different components imply that only one species of rotamers exists in a polymer film. Thus, only one rotamer seems to exist when 6-HQ is doped in a polymer film of PMMA or PVA, though the presence of both cis and trans rotamers was confirmed in a supersonic jet. It was shown that a cis rotamer is more stable than trans rotamer in a jet.¹⁵ Unfortunately, however, the stable form that can be taken in a small cavity of the polymer films could not be confirmed.

6. Conclusions

Polarized electroabsorption (E-A) spectra of 6-HQ doped in a polymer film of PMMA and PVA have been measured by using Stark absorption spectroscopy. E-A spectra of 6-HQ doped in PMMA and in PVA have been also measured as a function of temperature in the range of 50–300 K. It was found that E-A spectra of 6-HQ doped in PMMA markedly depend on temperature, whereas the shape of the E-A spectra of 6-HQ doped in PVA is essentially independent of temperature. The polarization dependence as well as the temperature dependence of the E-A spectra shows that 6-HQ is aligned along the applied electric field in PMMA at room temperature, whereas 6-HQ is not oriented along the electric field in PVA. As the temperature decreases, molecular orientation induced by an electric field is restricted even in PMMA. Thus, 6-HQ is mobile in PMMA at room temperature, whereas it is immobile in PVA even at room temperature, indicating that orientational polarizability is very sensitive to the surrounding environment. Spectral shift as well as spectral broadening has been observed in the presence of electric fields, and the magnitude of the change in electric dipole moment and in molecular polarizability between the ground state and the photoexcited states at room temperature have been determined. The molecular orientation in a polymer film in the presence of electric field appears to depend on the hydrogen bonding strength between 6-HQ and polymer; 6-HQ is very sensitive to the environmental conditions. The activation energy for the molecular orientation in PMMA has been estimated to be $\sim 260 \text{ cm}^{-1}$.

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