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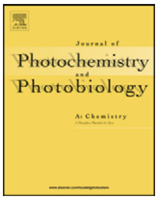

Electric field effects on state energy and molecular orientation of 2-hydroxyquinoline in solid polymer films

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ABSTRACT

External electric field effects on the electronic absorption spectra have been examined for 2-hydroxyquinoline (2-HQ) doped in polymer films of poly(methyl methacrylate) (PMMA) and poly(vinyl alcohol) (PVA). The electroabsorption (E-A) spectra of 2-HQ observed at 295 K and at 50 K show the change both in the permanent dipole moment ($\Delta\mu$) and in the molecular polarizability ($\Delta\alpha$) associated with the absorption transitions to the lower lying electronic states. The polarization dependence and the temperature dependence of the E-A spectra show that 2-HQ is oriented along the direction of applied electric fields at room temperature both in PMMA films and in PVA films. At a low temperature of ~50 K, on the other hand, the field-induced orientation of 2-HQ is restricted in both films, and only the Stark shifts induced by changes in $\Delta\mu$ and $\Delta\alpha$ are observed. 6-Hydroxyquinoline (6-HQ) also orients along the applied electric field in PMMA, but the field-induced orientation of 6-HQ is restricted in PVA even at room temperature [M.S. Mehata, T. Iimori, T. Yoshizawa, N. Ohta, J. Phys. Chem. A 110 (2006) 10985]. The difference of the field-induced orientation in PVA between 2-HQ and 6-HQ suggests that 2-HQ has a *cis enol* form in the ground state.

1. Introduction

The electrostatic interaction among charged and polar molecules or functional groups plays an important role in biological systems, which leads to particular biophysical molecular recognitions or molecular assembly formations. Among the biologically important molecules, the bifunctional hydroxyquinolines which undergo an excited-state charge transfer and subsequent proton transfer following photoexcitation have attracted much attention [1–11].

As reported in our previous paper [12], we examined the external electric field effects on absorption spectra of 6-hydroxyquinoline (6-HQ) doped in a polymer film of poly(methyl methacrylate) (PMMA) or poly(vinyl alcohol) (PVA) to elucidate the electronic structure as well as the dynamics in the electronically excited state of this molecule. It was shown that the state energy of 6-HQ is affected by an electric field in polymer matrices because the permanent dipole moment and molecular polarizability in the ground state of this molecule are different from the ones in the excited state. It was also shown that 6-HQ shows a molecular orientation along the field direction at room temperature in the presence of external electric fields even when 6-HQ was confined in a polymer matrix of PMMA. Further, it was shown that the field-induced molecular orientation of 6-HQ was restricted even at room temperature, when 6-HQ was confined in a polymer matrix of PVA. Then, it is interesting to know whether the polymer matrix dependence of the field-induced orientation, i.e., the difference between the field-induced orientation in PMMA and that in PVA results from the difference in hydrogen-bond interaction between solute and polymer matrix or from the difference in size of the free volume of the polymer matrix between PMMA and PVA.

In 6-HQ as well as in 5- or 7-hydroxyquinoline, intramolecular hydrogen-bond is not allowed because of a long distance between the –OH- and –N-functional groups. In these molecules, therefore, intermolecular hydrogen-bonds play a dominant role in structural formation and in dynamics in the ground state and in the excited states. For example, hydrogen-bonded complexes with water/alcohol/acetic acid molecules or other polar groups of the surroundings are easily formed in the ground state as well as in the excited state, and the excited-state proton transfer reaction may request participation of protic solvent molecules [13]. In 2-hydroxyquinoline (2-HQ), on the other hand, the –OH- and –N-functional groups are in close proximity, and an intramolecular hydrogen-bond may be formed. If the strength of the interaction between hydroxyquinoline and polymer matrix plays an important role in the electric-field-induced orientation of 6-HQ, therefore,

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the electric-field-induced orientation whose behaviour is different from each other between 2-HQ and 6-HQ may be observed. Hereafter hydrogen-bond is denoted by H-bond.

In the present study, we have measured the electroabsorption (E-A) spectra of 2-HQ doped in PMMA films and in PVA films. Based on the polarization dependence and the temperature dependence of the E-A spectra, electric field effects on the state energy and on the molecular orientation of 2-HQ are discussed, and a comparison is made between 6-HQ and 2-HQ. It was reported that 2-HQ can exist in *enol* and *keto* forms [7–11]; the enol form is more stable in the gas phase, whereas the keto form is more stable in solution especially in polar solvents owing to the stabilization of a zwitterionic resonance structure. The *enol* form of 2-HQ can undergo *cis* to *trans* isomerization. In the analysis of the E-A spectra of 2-HQ, therefore, a possibility was considered that different conformers of 2-HQ exist in polymer films.

2. Experimental

The procedure of the sample preparation is the same as the one reported previously [12]. PMMA and PVA films containing 2-HQ (1 mol%) (Aldrich) were prepared by a spin coating technique on a silica glass plate precoated with a conductive indium-tin-oxide (ITO) layer. A semitransparent aluminum film was deposited on the polymer film by a vacuum vapor deposition technique. The concentration of 2-HQ was 1 mol% relative to the monomer unit of PMMA or PVA. The thickness of the thin layer of 2-HQ doping PMMA or PVA, which was measured with an interferometer microscope, was typically 1.6 μm in PMMA and 1.8 μm in PVA.

Absorption measurements were performed with a Hitachi U-3500 spectrophotometer. E-A spectra were measured with the apparatus which is essentially the same as the one reported previously [14]. A conversing light beam form Xenon lamp of Jasco FP-777 spectrofluorometer was collimated and directed through an α-barium borate (α-BBO) polarization prism (CASIX, JDSU) and through the sample slide on an external photomultiplier, which was further amplified and divided into two channels. The dc component of the transmitted light intensity was directly collected by a computer, and the ac component synchronized with the applied voltage was recorded by a lock-in amplifier (SR830, SRS) at the second harmonic of the modulation frequency of the applied electric field. The amplitude and the phase signals from the output of the lock-in amplifier ($\Delta I(2\nu)$) were finally digitized and recorded by the computer together with the dc component.

The E-A spectra of 2-HQ were obtained at the normal angle and at the magic angle between the direction of the applied electric field and the electric vector of the excitation light. To change the angle χ, we rotated the sample holder following Snell's law, which depends on the refractive index of host polymers. Note that the refractive index of PMMA and PVA is 1.544 and 1.506, respectively [15,16]. The change in absorption intensity caused by the application of an electric field 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 equivalent dc signal. The details of the measurements of the polarized absorption and E-A spectra were described elsewhere [15].

The temperature dependence of the E-A spectra was examined with a non-polarized light at the normal incident angle in a range of 295–50 K in vacuo. 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 Inst., model 9600) with a silicon diode thermometer (Scientific Int., Si410A) [17].

3. Theory of electric field modulation spectroscopy

Molecular energy levels are influenced by an external electric field ($\boldsymbol{F}$), depending on the molecular parameters, i.e., electric dipole moment, μ, and molecular polarizability, α, of the state concerned. The Stark effect, i.e., the shift in transition energy (ΔE) due to an externally applied electric field, $\boldsymbol{F}$, is given by

$$\Delta E = -\Delta\mu \boldsymbol{F} - \frac{1}{2}\mathbf{F}\Delta\alpha\boldsymbol{F} \tag{1}$$

Here, $\Delta\mu$ and $\Delta\alpha$ are the differences in the dipole moment vector and molecular polarizability tensor, respectively, between the ground and excited states i.e., $\Delta\mu = \mu_e - \mu_g$, and $\Delta\alpha = \alpha_e - \alpha_g$.

By assuming an isotropic distribution of the molecules in PMMA and PVA films, the change in absorption intensity (ΔA) as a function of wavenumber, ν, in the presence of F, i.e., $\Delta A(\nu)$, can be expressed as a sum of the zeroth, first and second derivatives of the absorption spectrum as follows [18–21].

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

where $F = |\boldsymbol{F}|$, ν is the energy in wavenumber and f is the internal field factor. The coefficients of the derivatives, i.e., A_χ, B_χ and C_χ are associated with molecular properties of the systems. When molecules are fixed, A_χ is related to the change in the transition moment and orientational anisotropy upon application of an applied field, B_χ is associated with the change in the polarizability and C_χ is associated with the change in the permanent dipole moment. By neglecting the field-induced change in the transition moment polarizability and hyperpolarizability, the coefficients A_χ, B_χ and C_χ can be expressed as follows:

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

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

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

In the above equations, h represents the Planck's constant, c is the speed of light and T is the temperature, and $\bar{\mu}$ 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. η is the angle between the direction of $\Delta\mu$ and the transition dipole moment. ξ is the angle between μ_g and the transition dipole moment, and γ is the angle between $\Delta\bar{\mu}$ and μ_g. $\Delta\bar{\mu}$ and $\Delta\bar{\alpha}$ are given by the following equations:

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

In Eqs. (3) and (4), the temperature dependent terms are useful to understand the molecular orientation in the presence of applied electric field because these terms arise from the field-induced orientation [21].

4. Results

The absorption and polarized E-A spectra of 2-HQ doped in polymer films of PMMA or PVA were measured at room temperature

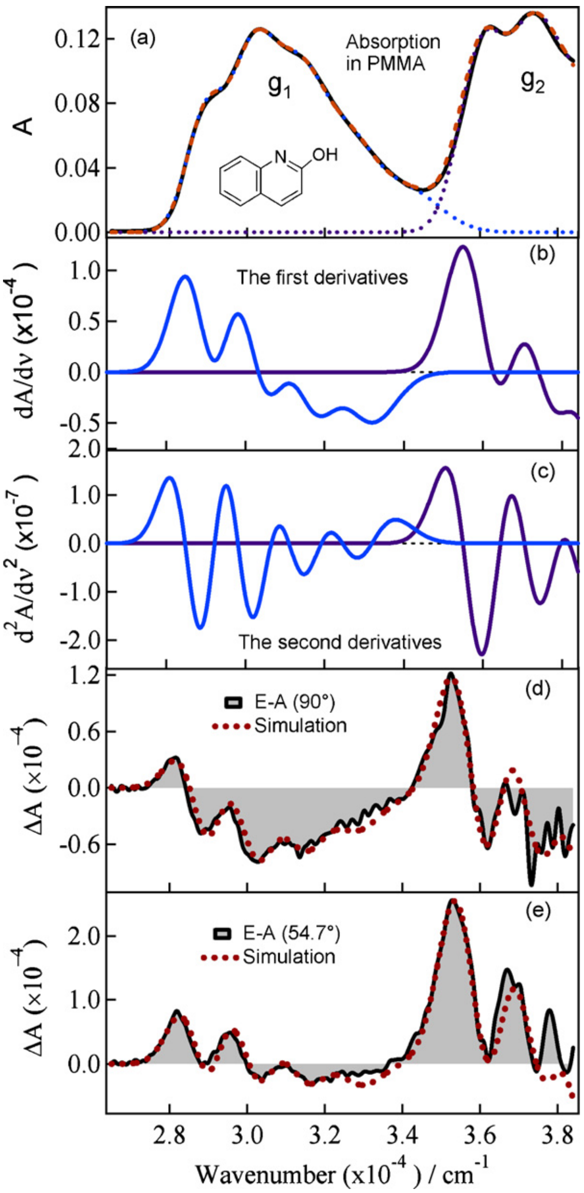


Fig. 1. (a) Absorption spectrum of 2-HQ doped in a PMMA film at a concentration of 1 mol% at room temperature (solid line), bands g_1 and g_2 (thin dotted line), their superposition (thick dotted line); (b) the first derivative and (c) the second derivative of the g_1 and g_2 absorption bands; (d) E-A spectrum observed at room temperature with $\chi = 90^\circ$ (shaded), together with the simulated spectrum (dotted line); (e) E-A spectrum observed at room temperature with $\chi = 54.7^\circ$ (shaded), together with the simulated spectrum (dotted line). The applied electric field strength was 0.7 MV cm^{-1}.

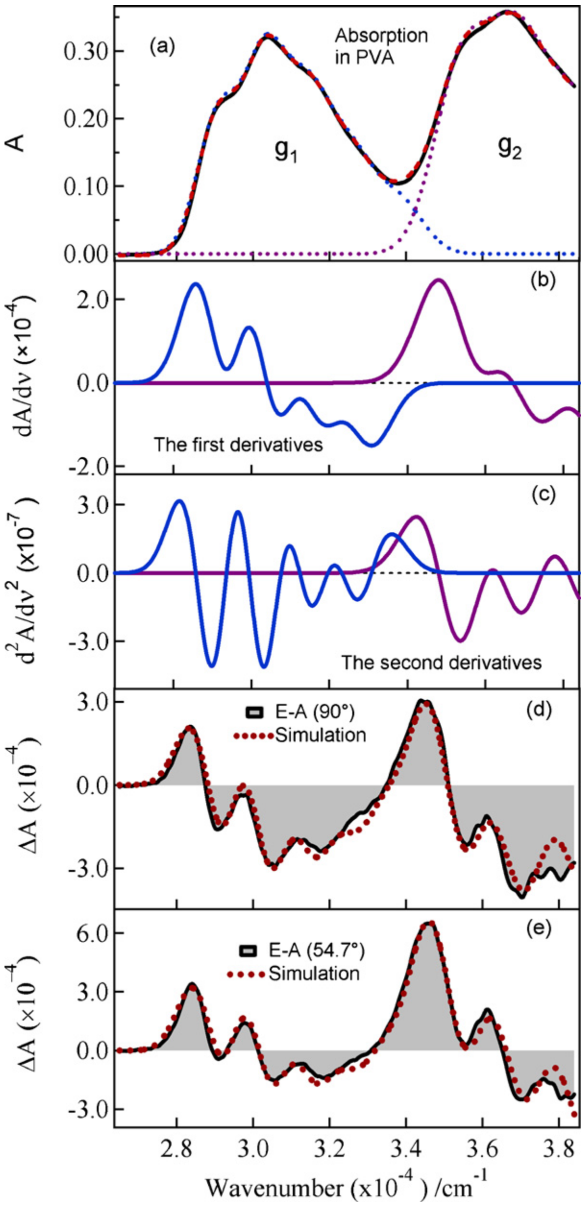


Fig. 2. (a) Absorption spectrum of 2-HQ doped in a PVA film at a concentration of 1 mol% at room temperature (solid line), bands g_1 and g_2 (thin dotted line) and their superposition (thick dotted line); (b) the first derivative and (c) the second derivative of the g_1 and g_2 absorption bands; (d) E-A spectrum observed at room temperature with $\chi = 90^\circ$ (shaded), together with the simulated spectrum (dotted line); (e) E-A spectrum observed at room temperature with $\chi = 54.7^\circ$ (shaded), together with the simulated spectrum (dotted line). The applied electric field strength was 0.7 MV cm^{-1}.

under the atmospheric conditions. The polarized E-A spectra were measured with a field strength of 0.7 MV cm^{-1}. Measurements were also carried out at different temperatures in vacuo.

Fig. 1 shows the absorption and E-A spectra of 2-HQ doped in a PMMA film, together with the first and second derivatives of the absorption spectrum. These spectra were measured at room temperature with the normal incident angle, i.e., $\chi = 90^\circ$ and magic angle, i.e., $\chi = 54.7^\circ$ in the region from 26,500 to 38,400 cm^{-1}. Similar experiments were carried out for 2-HQ doped in a PVA film. The results are shown in Fig. 2. The absorption spectra of 2-HQ doped in PMMA as well as in PVA exhibit two strong bands in the region from 26,500 to 38,400 cm^{-1}. As shown in Figs. 1a and 2a, the absorption spectra are reproduced by a superposition of two absorption bands, i.e., g_1 and g_2, which probably correspond to the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transition of 2-HQ, respectively. In PMMA, the absorption maxima of the g_1 and g_2 bands are at 30,320 and 37,411 cm^{-1}, respectively. Both bands show a blue shift (~80 cm^{-1}) in PVA. In PMMA, the g_1 band exhibits two shoulders at ~28,926 and ~31,400 cm^{-1}, and the g_2 band also shows a shoulder at 36,233 cm^{-1}, which is assigned to the vibronic structure. A similar structure was observed in the absorption spectrum of 2-HQ in PVA. The shape and the intensity maximum of these absorption spectra are similar to the ones in solution [11]. It may be important to note that the origin for the π–π^* transition of *keto* and *enol* forms was reported to be 29,112 and 31,349 cm^{-1}, respectively [9].

As shown in Fig. 1, the observed E-A spectra were simulated by a linear combination of the zeroth, first and second derivatives of the absorption spectrum, as expected from Eq. (2). In the whole region,

Table 1
Fitted parameters used to simulate the E-A spectra of 2-HQ doped in PMMA and PVA films at a temperature of 295 or 50 K.

Polymer	Absorption band	A_χ (MV^{-2})			B_χ (cm^{-1} MV^{-2})			C_χ (cm^{-2} MV^{-2})		
		90°		54.7°	90°		54.7°	90°		54.7°
		295 K	50 K	295 K	295 K	50 K	295 K	295 K	50 K	295 K
PMMA	g_1	-9.59×10^{-4} (-2.04×10^{-4})	0.0	4.08×10^{-5}	0.612 (0.204)	0.142	1.04	286 (163)	234	362
	g_2	-3.46×10^{-4} (-2.44×10^{-4})	0.0	7.14×10^{-4}	1.800 (0.470)	0.306	2.84	592 (285)	428	652
PVA	g_1	−0.00122 (−0.0004)	0.0	2.04×10^{-4}	1.938 (0.80)	0.360	2.122	469 (220)	240	448
	g_2	−0.00106 (−0.0004)	0.0	4.08×10^{-4}	2.918 (1.14)	0.360	4.081	1254 (560)	580	1836

The values given in parentheses are obtained under vacuum condition.

the E-A spectra are well simulated with the derivative spectra of each of the g_1 and g_2 absorption bands (Figs. 1d and 1e). Then, the coefficients of the zeroth, first and second derivatives, i.e., A_χ, B_χ and C_χ of Eq. (2) were obtained for the g_1 and g_2 band, respectively, at two different angles. These results are shown in Table 1. It is immediately noticed that the coefficients A_χ, B_χ and C_χ markedly depend on the angle χ.

The E-A spectra of 2-HQ in a PVA film measured at different angels of χ at room temperature could be similarly simulated by a linear combination of the zeroth, first and second derivative components of the absorption spectrum. E-A spectra observed with $\chi = 90°$ and with $\chi = 54.7°$ are shown in Fig. 2. The zeroth, first and second derivative coefficients of 2-HQ in PVA obtained for the g_1 and g_2 bands are also shown in Table 1. As in PMMA, these coefficients in PVA depend on χ. In both films, the zeroth derivative coefficient is negative at the normal incidence angle and positive at the magic angle, and the magnitude of the latter is much smaller than the former. Thus, the E-A spectra observed at the normal incidence and at the magic angle of χ are different from each other both in PMMA and in PVA, which is very different from 6-HQ. As reported in our previous paper [12], the E-A spectra of 6-HQ in PMMA significantly depend on χ, whereas the E-A spectra in PVA are independent of χ.

The E-A spectra of 2-HQ doping PMMA and PVA were measured at 50 K with $\chi = 90°$. The results are shown in Fig. 3, together with the absorption spectrum and its derivative spectra. The E-A spectra of 2-HQ at 50 K are very different from those at 295 K both in PMMA and in PVA. As described above, the E-A spectra of 2-HQ at 295 K could be simulated by a linear combination of the zeroth, first and second derivatives of the absorption spectrum both in PMMA and in PVA. On the other hand, the E-A spectra of 2-HQ at 50 K could be simulated by a linear combination of the first and second derivatives of the absorption spectrum both in PMMA and in PVA, and the zeroth derivative component was not necessary for the simulation, as shown in Fig. 3. The coefficients of B_χ and C_χ for the g_1 and g_2

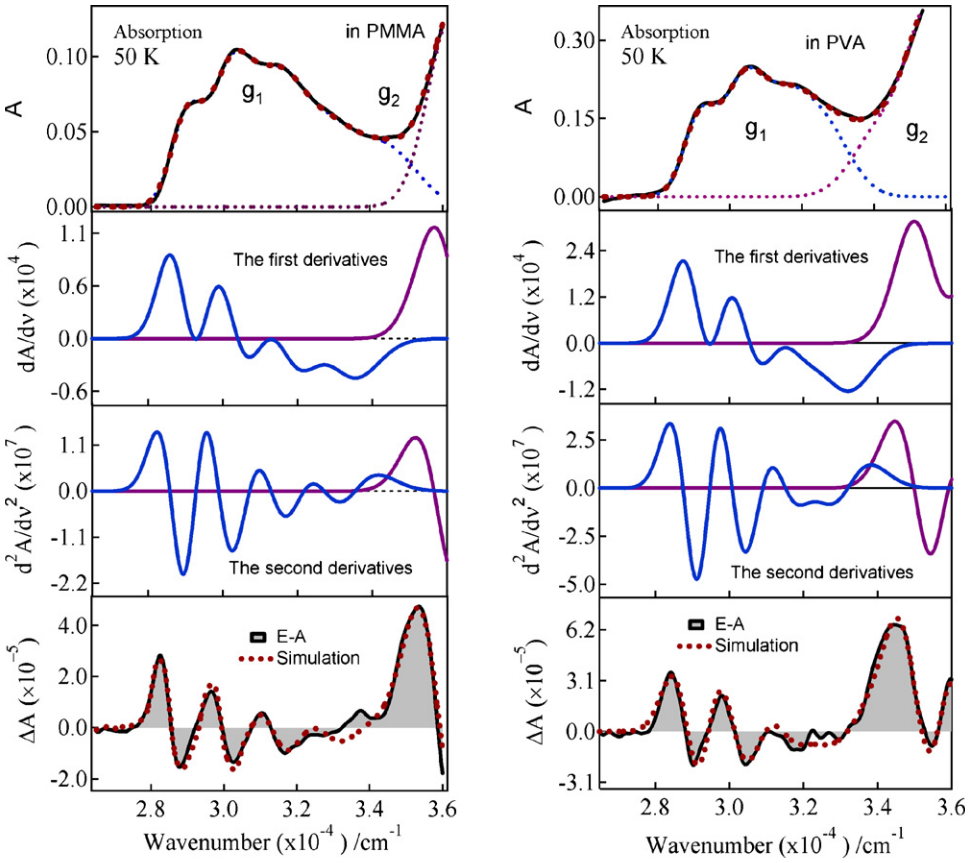


Fig. 3. Absorption spectra (top) and E-A spectra (bottom) of 2-HQ doped in a PMMA film (left) and in PVA film (right) at a concentration of 1 mol% observed at a temperature of 50 K. Two absorption bands i.e., g_1 and g_2, their superposition (thick dotted line) are shown in the top. The first and second derivative spectra of the g_1 and g_2 absorption bands are shown in the middle, separately, and the simulated spectra of the E-A spectra are also shown in the bottom by a dotted line. The applied electric field strength was 0.7 and 0.5 MV cm^{-1} in PMMA and PVA films, respectively.

Table 2
Molecular parameters obtained from the E-A spectra of 2-HQ doped in polymer films at a temperature of 295 or 50 K. The subscripts 1 and 2 correspond to the g_1 and g_2 states, respectively.

Polymer	$\Delta\bar{\mu}_1$/D		$\Delta\bar{\mu}_2$/D		$\Delta\bar{\alpha}_1$/Å^3		$\Delta\bar{\alpha}_2$/Å^3	
	295 K	50 K	295 K	50 K	295 K	50 K	295 K	50 K
PMMA	2.77 ± 0.15	2.23 ± 0.10	3.72 ± 0.3	3.01 ± 0.3	30 ± 2	5 ± 2	86 ± 5	11 ± 4
PVA	3.07 ± 0.10	2.25 ± 0.15	6.24 ± 0.6	3.51 ± 0.1	74 ± 4	12 ± 3	143 ± 4	12 ± 3

The reported values are not corrected for the internal field factor, i.e., *f*.

bands determined from the simulation of the E-A spectra of 2-HQ at 50 K are given in Table 1.

5. Discussion

When external electric fields are applied to 2-HQ doped in a polymer film, it is expected that the absorption spectra show shift and broadening, which gives rise to the first and second derivatives of the absorption spectrum, respectively, because of the difference in permanent dipole moment ($\Delta\mu$) and molecular polarizability ($\Delta\alpha$) between the ground and excited electronic states. Additionally, 2-HQ which has the permanent dipole moment in the ground state may have a tendency to show an anisotropic orientation of the molecules in the presence of electric fields, unless molecules are fixed in a matrix. It is unlikely that molecules can rotate freely in polymer matrices, but a rotation with a small angle may be expected. In fact, we reported the field-induced molecular orientation of 6-HQ, indole and its methyl-derivative in a PMMA polymer matrix at room temperature, which is much below the glass transition temperature (T_g), based on the polarization measurements of the E-A spectra. Note that the T_g of PMMA and PVA matrices are 378 and 358 K, respectively [22,23].

At a low temperature of 50 K, the E-A spectra observed in PMMA and PVA are quite similar in shape to the second derivative of the absorption spectrum (see Fig. 3), indicating that $\Delta\mu$ between the ground and the excited states is very significant for the E-A spectra. As described above, however, the E-A spectra at 50 K could be reproduced by a linear combination of the first and second derivative components of the absorption spectrum, indicating the not only $\Delta\mu$ but also $\Delta\alpha$ are significant between the ground state and the excited states.

It is worth mentioning that the zeroth derivative contribution is negligible at 50 K, i.e., $A_\chi = 0$, both in PMMA and in PVA (see Table 1). The results show that the molecular orientation of 2-HQ molecules is completely restricted at 50 K; molecules are immobilized in polymer films. Then, the values of $\Delta\bar{\alpha}$ as well $\Delta\bar{\mu}$ can be estimated, based on Eqs. (4) and (5). The results are shown in Table 2.

The polarized E-A spectra of 2-HQ at 295 K are quite similar in shape to the first derivative of the absorption spectrum especially at the magic angle of χ (see Figs. 1 and 2), indicating that the field-induced change in the absorption spectrum mainly comes from the change in the polarizability following the absorption transition. Actually, the zeroth and the second derivatives of the absorption spectrum are necessary to reproduce the E-A spectra (see Table 1). The contribution of the zeroth derivative component is very large in the E-A spectra at 295 K with $\chi = 90^\circ$ (see Table 1), which is very different from the one at 50 K. These results suggest that a field-induced orientation occurs both in PMMA and in PVA at room temperature. The magnitude of $\Delta\bar{\mu}$ and $\Delta\bar{\alpha}$ determined from the coefficient of B_χ and C_χ in PMMA and in PVA at 295 K are shown in Table 2 for both g_1 and g_2 bands. When $\chi = 54.7^\circ$, the zetroth derivative component must be zero even when the field-induced molecular orientation occurs, according to Eq. (3). As shown in Table 1, however, the zeroth derivative component cannot be neglected to reproduce the E-A spectra at room temperature even at $\chi = 54.7^\circ$. These results are different from the ones at 50 K, where the zeroth derivative component is negligible. Though the zeroth derivative component cannot be neglected, however, the zeroth derivative component is much smaller at $\chi = 54.7^\circ$ than that at $\chi = 90^\circ$ both in PMMA and in PVA, which supports the field-induced orientation along the applied electric field in both films at room temperature. At the moment, it is not known why the zeroth derivative component is not negligible at room temperature even with $\chi = 54.7^\circ$.

Based on the χ dependence of Eq. (5), i.e., from the difference in E-A spectra between $\chi = 90^\circ$ and $\chi = 54.7^\circ$, the angle (η) between the transition dipole moment and the change in the permanent dipole moment was evaluated. The results are shown in Table 3. These values are very different from each other in PMMA and PVA. It is noted that the direction of the optical transition moment of *cis enol* 2-HQ was reported from the calculation to be ±39° relative to the direction of the inertial axis [8].

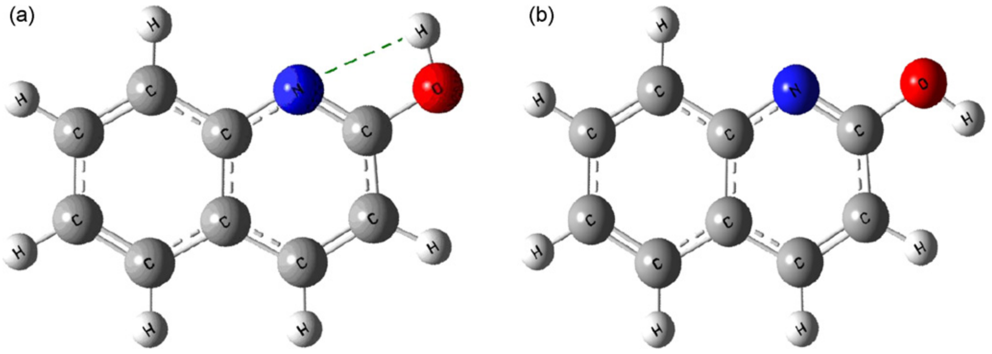
The magnitude of $\Delta\bar{\mu}$ at 50 K, where the field-induced orientation of 2-HQ is restricted, is close to the one at room temperature. However, the value of $\Delta\bar{\alpha}$ at 50 K is much smaller than that at 295 K. This is probably because $\Delta\bar{\alpha}$ at 295 K consists of the change in the electronic polarizability and orientational polarizability, and the value of $\Delta\bar{\alpha}$ at 50 K shown in Table 2 may result from the molecular polarizability, not from the orientational polarizability.

$\Delta\bar{\mu}$ as well as $\Delta\bar{\alpha}$ in PMMA may be the same as in PVA, if the interaction between polymer matrix and 2-HQ is the same. Then, the difference between $\Delta\bar{\alpha}$ in PMMA and in PVA at 295 K may give the difference in the orientational polarizability between both polymers, which probably comes from the difference in the hydrogen-bonding ability and/or polarity between PMMA and PVA. The interaction between polymer matrix and 2-HQ may significantly modify the ground state dipole moment of the polar chromophore resulting in the change both in $\Delta\bar{\mu}$ and in the orientational polarizability. Apart form this, it is expected that PVA has a larger free volume and possible less rigidity than PMMA [2], which may be related to the larger value of A_χ in PVA than in PMMA. In fact, the matrix dependence of $\Delta\bar{\mu}$ and $\Delta\bar{\alpha}$ were reported for the all-trans-retinal, i.e., between polymers of PMMA and polyethylene [24,25].

The E-A spectra of hydroxyquinolines show a different matrix dependence from each other, when the position of OH functional group is different in the quinoline ring. For example, E-A spectra of 6-HQ in PMMA are very different from those in PVA at room temperature, as already reported in our previous paper [12], whereas E-A spectra of 2-HQ are similar to each other in both matrices, as shown in Figs. 1 and 2. The E-A spectra of 6-HQ in PMMA show the significant contribution of the zeroth derivative component at room temperature. When the temperature is as low as 50 K, the contribution of A_χ completely vanishes, and the E-A spectrum became close

Table 3
The angle η between the directions of $\Delta\mu$ and the transition dipole moment. The subscripts 1 and 2 correspond to the g_1 and g_2 states, respectively.

Polymer	η_1	η_2
PMMA	34°	45°
PVA	59°	21°



Scheme 1. B3LYP/6-31G(d,p) minimum energy structures of *cis* (a) with an extra added dotted green line) and *trans* (b) forms of 2-HQ.

in shape to the second derivative of the absorption spectrum, which is quite similar to 2-HQ. In PVA, on the other hand, the E-A spectra of 6-HQ have no contribution of the zeroth derivative component even at room temperature and are independent of the temperature, which is very different from 2-HQ. Based on these results, it was concluded that 6-HQ could be oriented along the applied electric field in PMMA, whereas the field-induced orientation of 6-HQ was restricted in PVA at room temperature. In contrast with 6-HQ, 2-HQ can be oriented along the applied electric field direction both in PMMA and in PVA at room temperature, though the orientation of 2-HQ is restricted at a low temperature of 50 K both in PMMA and PVA films.

It is interesting to know whether there is some evidence in absorption and E-A spectra with respect to the existence of 2-HQ in its different forms, since both *cis* and *trans* forms give almost similar stabilization energy in the ground state. The observed E-A spectra of 2-HQ could be well fitted with the g_1 and g_2 absorption bands, clearly indicating the presence of only one form of 2-HQ in PMMA as well as in PVA films. If the absorption bands of the different species overlap, it is unlikely that the E-A spectra can be simulated by taking the derivative components of the observed absorption spectrum. Therefore, the present E-A spectra seem to rule out the existence of two different forms of 2-HQ. As a single species of 2-HQ, *cis enol* form where O–H bond can be taken is considered (see dotted line in Scheme 1), since a formation of the intramolecular H-bond between the hydroxy hydrogen and the ring nitrogen atom seems to be essential to interpret the present results, as will be mentioned below. It is noted that the intramolecular H-bond cannot be formed between two functional groups in *trans enol* rotamer of 2-HQ (cf. structure of *cis* and *trans* rotamers of Scheme 1).

Due to the presence of the intramolecular H-bond, *cis enol* form of 2-HQ cannot form intermolecular H-bond even in the PVA polymer (or the intermolecular H-bond is weak enough) and hence *cis enol* form of 2-HQ appears to be free for the motion/reorientation within the available free volume of PMMA as well as PVA in the presence of electric fields. Thus, the intramolecular H-bond in 2-HQ appears to be stronger than the intermolecular H-bond between 2-HQ and polymer matrix. Probably this is the reason why the field-induced orientation occurs for 2-HQ both in PMMA and in PVA at room temperature. Note that PMMA is a weaker H-bonding polymer than PVA. In fact, the presence of the intramolecular H-bond in the *cis enol* form of 2-HQ was confirmed in the vapor phase by the observation of the perpendicular displacement of the hydroxy hydrogen [8]. In contrast with 2-HQ, the intermolecular H-bond may be formed between 6-HQ and the polymer matrix since two functional groups in 6-HQ are far apart from each other (∼10 Å), which cannot allow to form the intramolecular H-bond in *cis*/or *trans* rotamer. Then, it may be reasonable to consider that 6-HQ forms the intermolecular H-bond with the functional groups of PVA, which restricts the field-induced orientation of 6-HQ in PVA films in the presence of electric fields. In PMMA, it appears that 6-HQ does not form the intermolecular H-bond or that the intermolecular H-bond is not strong enough to prevent reorientation of 6-HQ in the presence of electric fields.

6. Summary

The polarized E-A spectra of 2-HQ doped in PMMA and in PVA were measured at room temperature with different angles between the electric vector of the excitation light and the applied electric field, i.e., at the normal incident case and at the magic angle case. The E-A spectra of 2-HQ doped in PMMA and PVA films have also been measured at different temperatures, i.e., at 295 and 50 K. Spectral shifts as well as spectral broadenings have been observed in 2-HQ, indicating a significant change in the electric dipole moment ($\Delta\mu$) and in the polarizability ($\Delta\alpha$) following photoexcitation. The polarization dependence and the temperature dependence of the E-A spectra clearly show the field-induced orientation of 2-HQ in a cavity of PMMA and PVA in the presence of electric fields at room temperature. 6-HQ is also oriented along the applied field direction in PMMA, but 6-HQ is not oriented along the electric field in PVA even at room temperature, in contrast with 2-HQ, presumably due to the intermolecular H-bond. The fact that the E-A spectra could be well fitted with the derivative spectra of the observed absorption spectrum, together with the presence of the reorientational effects in both polymers, suggests only the existence of *cis enol* form of 2-HQ. The *cis enol* form of 2-HQ may be stabilized by the intramolecular H-bond between the hydroxy hydrogen and nitrogen atom.

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References

[1] J. Konijnenberg, G.B. Ekelmans, A.H. Huizer, C.A.G.O. Varma, J. Chem. Soc. Faraday Trans II 85 (1989) 39.
[2] M.S. Mehata, H.C. Joshi, H.B. Tripathi, Spectrochem. Acta A 58 (2002) 1589–1598;
M.S. Mehata, H.C. Joshi, H.B. Tripathi, Spectrochem. Acta A 59 (2003) 559.
[3] O. Poizat, E. Bardez, G. Buntinx, V. Alain, J. Phys. Chem. A 108 (2004) 1873.
[4] M.S. Mehata, H.C. Joshi, H.B. Tripathi, Chem. Phys. Lett. 366 (2002) 628;
M.S. Mehata, H.C. Joshi, H.B. Tripathi, Chem. Phys. Lett. 359 (2002) 314.
[5] C. Tanner, C. Manca, S. Leutwyler, Science 302 (2003) 1736.

[6] M.S. Mehata, Chem. Phys. Lett. 436 (2007) 357–361;
M.S. Mehata, J. Phys. Chem. B 112 (2008) 8353.
[7] M.J. Cook, A.R. Katritzky, P. Linda, R.D. Tack, J. Chem. Soc., Perkin Trans. 2 (1973) 1080.
[8] A. Held, D.F. Pluquellic, J.L. Tomer, D.W. Pratt, J. Phys. Chem. 95 (1991) 2877.
[9] M.R. Nimlos, D.F. Kelley, E.R. Bernstein, J. Phys. Chem. 91 (1987), 6610 and reference cited therein.
[10] P. Beak, Acc. Chem. Res. 10 (1977) 186.
[11] M.S. Mehata, J. Instrum. Soc. Ind. 34 (2005) 249.
[12] M.S. Mehata, T. Iimori, T. Yoshizawa, N. Ohta, J. Phys. Chem. A 110 (2006) 10985.
[13] B. Bhattacharya, A. Samanta, J. Phys. Chem. B 112 (2008) 10101.
[14] S. Umeuchi, Y. Nishimura, I. Yamazaki, H. Murakami, M. Yamashita, N. Ohta, Thin Solid Films 311 (1997) 239.
[15] E. Jalviste, N. Ohta, J. Chem. Phys. 121 (2004) 4730.
[16] R. Kumar, A.P. Singh, A. Kapoor, K.N. Tripathi, Opt. Eng. 43 (2004) 2134.
[17] T. Iimori, A.M. Ara, T. Yoshizawa, T. Nakabayashi, N. Ohta, Chem. Phys. Lett. 402 (2005) 206.
[18] W. Liptay, in: E.C. Lim (Ed.), Excited States, vol. 1, Academic Press, New York, 1974, p. 129.
[19] G.U. Bublit, S.G. Boxer, Annu. Rev. Phys. Chem. 48 (1997) 213.
[20] N. Ohta, Bull. Chem. Soc. Jpn. 75 (2002) 1637.
[21] E. Jalviste, N. Ohta, J. Photochem. Photobiol. C 8 (2007) 30.
[22] J. Barandrup, E.H. Immergut (Eds.), Polymer Handbook, John Wiley & Sons, New York, 1975.
[23] O. Probst, E.M. Moore, D.E. Resasco, B.P. Grady, Polymers 45 (2004) 4437.
[24] A. Chowdhury, S.A. Locknar, L.L. Premvardhan, L.A. Peteanu, J. Phys. Chem. A 103 (1999) 9614.
[25] S.A. Locknar, A. Chowdhury, L.A. Peteanu, J. Phys. Chem. B 104 (2000) 5816.