Effect of inhomogeneous band broadening on the nonlinear optical properties of hydrazones

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It is well known that an electroabsorption (EA) spectrum can be described as a linear combination of the zero-, first-, and second-order derivatives of an absorption spectrum on the basis of a theoretical formula derived by Liptay (Liptay equation). According to the Liptay equation, the coefficients of the zero-, first-, and second-order derivatives (these coefficients are abbreviated as D, F, and H terms, respectively) indicate the following three nonlinear optical properties of a material: (1) transition dipole-moment polarizability and its hyperpolarizability, (2) polarizability change upon photoexcitation ($\Delta\alpha$), and (3) static dipole-moment change upon photoexcitation ($\Delta\mu$). The Liptay equation can be applied only in the case when nonlinearity of an entire absorption band is supposed to be uniform. If this is not the case, for example, due to inhomogeneous band broadening, the nonlinear optical properties of the material cannot be simply derived from the D, F, and H values. In this study, we explicitly included the effect of inhomogeneous band broadening and reformulated the Liptay equation. On the basis of our formula, we analyzed the EA spectra of a series of hydrazones derived from biological polyenes. Even in the case when the effect of inhomogeneous band broadening is predominant, the nonlinearity of these hydrazones can be correctly evaluated.

I. INTRODUCTION

Pigments in biological systems are under the influence of electrostatic interactions within their surrounding protein environment and, hence, the physical properties of these pigments are often determined by these interactions. Therefore, in order to reveal the functional mechanisms of pigments in biological systems, it is necessary to determine to what extent and how their physical parameters are influenced by an externally applied electric field.[1,2] Optical absorption spectroscopy is one of the methods used to probe the physical characteristics of the pigments. An externally applied electric field causes a change in the absorption spectrum through the nonlinear optical properties of the pigments. The following six nonlinear optical properties play an important role in this change:[3–9] (1) the energies of optically forbidden states, (2) the energies of charge-transfer states, (3) the orientation of a molecule against applied electric field, (4) transition dipole-moment polarizability and its hyperpolarizability, (5) polarizability change upon photoexcitation ($\Delta\alpha$), and (6) dipole-moment change upon photoexcitation ($\Delta\mu$). In order to identify the physical parameters that contribute to the electrostatic interaction, it is crucial to correctly evaluate these properties of the pigment. Electroabsorption (EA) spectroscopy is a widely used method to detect an absorption change induced by exposure of applied electric field. The method of analysis of EA spectra has already been well established by Liptay.[10,11] According to his method, an absorption change $\Delta A(\nu)$, caused by exposure of externally applied electric filed, can be written as a linear combination of the zero-, first-, and second-order derivatives of an original absorption spectrum $A(\nu)$. If the angle between the direction of the applied electric field and the polarization of an incident radiation is set to be 54.7° (magic angle), this relation can be

given by Eq. (1). This formula is well known as the Liptay equation:

$$\Delta A(\nu) = \frac{1}{3}\left[DA(\nu) + F\nu\frac{d[A(\nu)/\nu]}{hd\nu} \right.$$
$$\left. + H\nu\frac{d^2[A(\nu)/\nu]}{2h^2d\nu^2} \right] E_{int}^2, \qquad (1)$$

$$D = 1/|\boldsymbol{M}|^2\sum_{ij}\ (X_{ii}X_{jj}+2M_iY_{ijj}), \qquad (2)$$

$$F = 1/2\mathrm{Tr}(\boldsymbol{\Delta\alpha}) + (2/|\boldsymbol{M}|^2)\cdot\left(\sum_{ij}\ M_iX_{ij}\right)\cdot\boldsymbol{\Delta\mu}, \qquad (3)$$

$$H = |\boldsymbol{\Delta\mu}|^2. \qquad (4)$$

Here, $\boldsymbol{M}$ is a transition dipole moment. X and Y are transition dipole-moment polarizablity and its hyperpolarizability, respectively. E_{int} is an internal electric field that relates to the externally applied electric field through a local-field correlation factor.

According to the Liptay equation, it is realized that the transition dipole-moment polarizability and its hyperpolarizability, as well as $\Delta\alpha$ and $\Delta\mu$ values, can be directly derived from the D, F, and H values (for simplicity we hereafter describe these three values as nonlinear coefficients). It is to be noted, however, that this equation implicitly assumes the uniform nonlinearity over an entire absorption band. Occasionally this assumption is not valid, in which case these nonlinear optical parameters cannot be directly determined.[12–14] As an example, Wortmann *et al.*[13] reported that the H term of a broad absorption band of tetraphenyl

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butatriene took a negative value, although the H value should always be positive according to Eq. (4); H is a square of $\Delta\mu$. They have successfully explained the cause of this discrepancy by assuming that the broad absorption band of the tetraphenyl butatriene is composed of two subbands with different nonlinearities. Another example is the study by Krawczyk and Olszówka on the EA spectroscopy of various symmetrical carotenoids.[14] They reported the presence of $\Delta\mu$ in these carotenoids, although they could not have dipole moment due to the symmetry reason. They successfully explained the cause of this contradiction by assuming that nonlinearity is not uniform over a single absorption band due to inhomogeneous band broadening. It is reported that inhomogeneous band broadening in carotenoids arises from molecular distortion caused by the twisting around C-C bonds.[15] Such conformational distortion may significantly affect the nonlinear optical properties of carotenoids.[14] Thus, the origin of the nonuniform nonlinearity is thought to be the intrinsic property of carotenoids. These findings are strongly suggestive of the nonuniform distribution of the nonlinearities over an absorption band. Especially in the case of molecules with polyene structure,[14] when absorption spectra are inhomogeneously broadened it is absolutely necessary to take into account the effect of nonuniformity of the nonlinearities in order to correctly understand the physical implications of EA spectra.

As mentioned above, Krawczyk and Olszówka revealed that inhomogeneous band broadening causes nonuniformity of the nonlinearities over a single absorption band.[14] Unfortunately, their treatment seems to be incomplete, since their discussion ignored the contribution of the D term. The importance of this particular term has been realized in three different kinds of materials: (1) transition-metal complexes, (2) photosynthetic pigment-protein complexes, and (3) hydrazones we have recently reported.[11,16–20] It is necessary to investigate the effect of inhomogeneous band broadening on the D term for the complete understanding of physical implications of EA spectra. The objective of this study is to reveal the effect of inhomogeneous band broadening on all the three nonlinear coefficients: D, F, and H terms. In the previous study, we found that the high-energy side absorption band of the hydrazones took negative H values. On the basis of our formula, we will explain the cause of this anomaly.

II. MATERIALS AND METHODS

A. Sample preparation

Figure 1 shows chemical structures of hydrazones derived from a series of polyenes. They were synthesized by simple condensation of the polyenes with 2,4-dinitrophenyl hydrazine (DNPH) in the presence of a catalytic amount of p-toluenesulfonate. The polyenes themselves were synthesized, starting from the shorter polyene units, by the use of Horner-Emons, Wittig, and Aldol reactions. For simplicity, we hereafter call them C15-, C17-, C18-, and C20-DNPH, respectively, according to the number of carbon atoms in the polyene part (see Fig. 1).
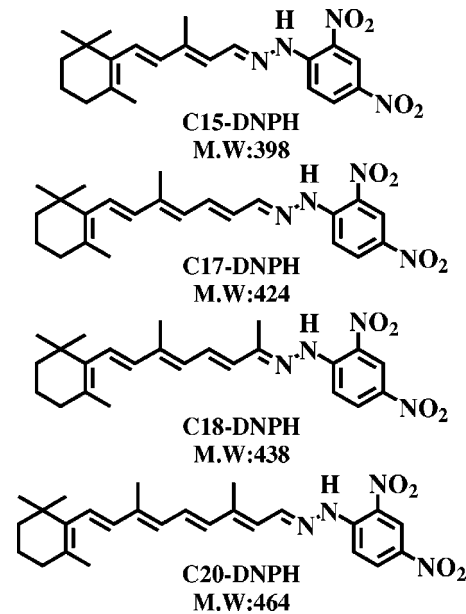

FIG. 1. Chemical structures of hydrazones derived from a series of biological polyenes.

B. Optical characterization

Detailed procedures to record the absorption and the electroabsorption spectra of hydrazones were described in Ref. 20, and we have reproduced these here briefly. The absorption and the EA spectra of spin-coated films of a methyl methacrylate polymer (PMMA polymer, Wako pure chemical industry) were recorded, in which the hydrazones were dispersed isotropically. The spin-coated films were formed on a surface of glass substrate where gold electrodes (gap distance is 60–150 μm) had been installed. Optical absorption spectra were recorded with an Otsuka MCPD-1000 spectrophotometer. EA spectra were recorded in the setup described below. Light from a 150 W Xe short-arc lamp (Hamamatsu, C7535) was dispersed by a monochromator (Acton Research, SpectraPro 150) and used to irradiate a sample cell. The incident radiation was linearly polarized using a Gran-Thompson prism and guided to the gap between the electrodes on the sample cell. The angle between the electric vector of the incident light and the electric field applied to the sample was set at 54.7° (magic angle). A sinusoidal ac voltage with a frequency $f = 500$ Hz generated by a function generator (NF, E-1201A) was amplified to a high voltage (40 kV/cm) through a high-voltage bipolar amplifier (NF, 4305). Light intensity transmitted through the sample was detected using a silicon photodiode (Hamamatsu, S1336-8BQ). The dc component of the signal was recorded on a digital multimeter (Fluke, 45), while the ac component was amplified by using a dual-phase lock-in amplifier (NF, 5610B). Among the changes (ΔI) of the transmitted light intensity (I) induced by the applied electric field with frequency f, only those with $2f$ frequency were selectively amplified by the lock-in amplifier. Absorbance changes ΔA induced by the applied electric field were calculated by using the following equation, $\Delta A = -\ln[(I+\Delta I)/I]/2.303$.
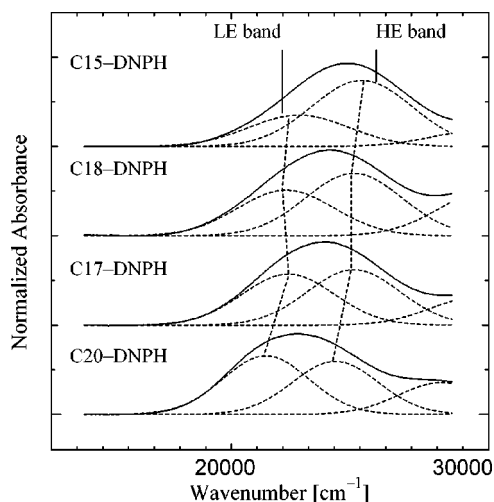
FIG. 2. The absorption spectra of the hydrazones. The solid lines indicate the experimentally observed absorption spectra. Dotted lines are Gaussian subbands that were determined as the result of the deconvolution of these spectra.

C. Semiempirical molecular-orbital calculation

In order to theoretically identify the absorption bands of the hydrazones, their transition energy, linear combination of atomic orbital (LCAO) coefficients, and oscillator strength of the hydrazones were semiempirically computed with MOPAC 2000 ver.1.11 and MOS-F ver.4.2c (Fujitsu Ltd.). Charge distributions of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital +1 (LUMO+1) and the $\Delta\mu$ values were also calculated for the evaluation of nonlinear optical parameters. Geometry optimization was performed by the use of MOPAC with AM1 Hamiltonian, which is considered to be the most reliable way to predict the stable structures of these biological polymers.[21–23] The electronic transitions, LCAO coefficients, the charge distributions, and the $\Delta\mu$ values for the optimized geometries were calculated by means of an INDO/CI (intermediate neglect of differential overlap/configuration-interaction) method using the MOS-F program.

III. RESULTS AND DISCUSSION

A. Linear and nonlinear optical properties of the hydrazones

Figure 2 shows experimentally observed absorption spectra (solid lines) of the hydrazones and several Gaussian subbands (dotted lines) that were determined as the result of deconvolution of these spectra. The absorption spectra were successfully deconvoluted into these subbands with reference to the results of INDO/CI molecular-orbital calculations (see Ref. 20 for detail). In the deconvolution, the bandwidths of the subbands in each hydrazone were set to be unique. The absorption spectrum of each hydrazone was mainly composed of two subbands. The lower energy (LE) band corresponds to the optical transition from HOMO to LUMO. The higher energy (HE) band corresponds to HOMO→LUMO +1 transition. According to the results of INDO/CI molecular-orbital calculations it was found that the electron distribution of the hydrazones is localized on the hydrazine
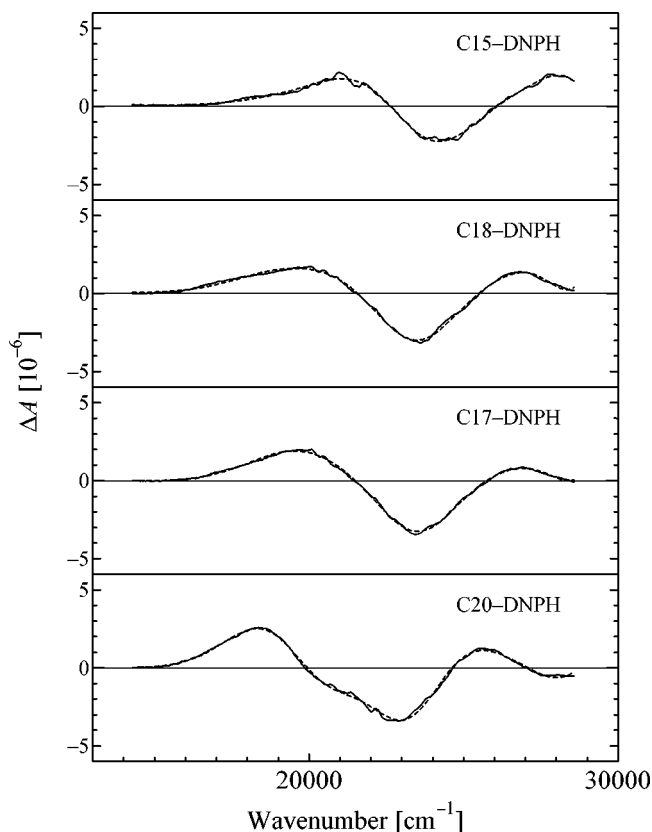

FIG. 3. Experimentally observed electroabsorption spectra (solid lines) and the results of the wave form analysis (dotted lines) of the hydrazones.

moiety (N-N part) in HOMO, and at the nitro-oxide group of the *ortho* and *para* positions, respectively, in LUMO and LUMO+1. This indicates that there are two transition dipoles along a molecular axis in the hydrazones.

Figure 3 shows EA spectra (solid lines) of the hydrazones and wave forms derived from the analyses of the EA spectra (dotted lines). The optical nonlinear parameters of the hydrazones were determined from these EA spectra. If the nonlinearity of a molecule were uniform across the whole absorption band, then the EA spectra should be reproducible by a linear combination of the zero-, first-, and second-order derivatives of the original absorption spectra. However, in this study such simple linear combinations could not reproduce the experimental EA spectra. Therefore it was necessary to assume that each subband has its own nonlinearity. By using the linear combinations of the three derivatives of the subbands, the observed EA spectra could then be satisfactorily reproduced as illustrated with dotted lines in Fig. 3.

The nonlinear coefficients (D, F, and H) of each subband were determined by means of a multiregression analysis. These coefficients, as well as the bandwidths of the LE and the HE bands of each hydrazone, are summarized in Table I. From these data two remarkable features are apparent: (1) both LE and HE bands have large transition dipole-moment polarizablity and hyperpolarizability (D factor), and (2) H values of the HE bands thus determined are always negative.

In the previous study,[20] we have already discussed the origin of the D factor. In this study, we will focus on the

TABLE I. Nonlinear parameters (D, F, and H) and the width (Σ) of the LE and HE bands.

	C15-DNPH		C18-DNPH		C17-DNPH		C20-DNPH	
	LE	HE	LE	HE	LE	HE	LE	HE
$D(10^{-17}\ (\mathrm{m/V})^2)$	3.6	-1.9	2.0	-1.8	1.3	-1.5	1.0	-1.5
$F(10^{-36}\ (\mathrm{C\,m^2/V}))$	-0.73	-0.42	-0.45	-0.39	-0.28	-0.31	-0.25	-0.31
$H(10^{-56}\ (\mathrm{C\,m})^2)$	1.1	-1.4	0.82	-1.4	0.61	-1.0	0.64	-0.99
$\Sigma\ (\mathrm{cm}^{-1})$	2754		2657		2535		2354	

explanation for the negative H values in order to complete the analysis of EA spectroscopy on hydrazones. Particular attention will be focused on the investigation of the effect of inhomogeneous band broadening on the nonlinear coefficients of the hydrazones.

B. Effect of inhomogeneous band broadening on D, F, and H values

In this section a generalized formulation about the effect of inhomogeneous band broadening upon nonlinearity is performed, based on the background originally developed by Krawczyk and Olszówka.[14] The experimentally observed absorption band, $A(\nu)$, is assumed to be an ensemble of a number of homogeneously broadened absorption bands, $A_0(\nu)$. $A_0(\nu)$'s are distributed within $A(\nu)$ according to a distribution function $\rho(\delta)$, where δ is the frequency shift from the peak frequency (ν_0) of the absorption band. In this model, $A(\nu)$ can be expressed as

$$A(\nu)=\int d\delta\rho(\delta)A_0(\nu-\nu_0-\delta). \qquad (5)$$

The change of the absorption band $\Delta A(\nu)$ upon exposure of an externally applied electric field can be written as a linear combination of the zero-, first-, and second-order derivatives of A_0, which is a similar expression to Eq. (1). While each nonlinear coefficient is supposed to take a constant value in Eq. (1), here all three nonlinear coefficients $D_i(\delta)$, $F_i(\delta)$, and $H_i(\delta)$ are described as functions of δ in order to include nonuniformity of nonlinearity due to inhomogeneous band broadening. In this model, the $\Delta A(\nu)$ can be written as

$$\Delta A(\nu)=\int d\delta\rho(\delta)\frac{1}{3}\left[D_i(\delta)A_0(\nu-\nu_0-\delta)\right.$$
$$+F_i(\delta)\nu\frac{d[A_0(\nu-\nu_0-\delta)/\nu]}{hd\nu}$$
$$\left.+H_i(\delta)\nu\frac{d^2[A_0(\nu-\nu_0-\delta)/\nu]}{2h^2d\nu^2}\right]E_{int}^2. \qquad (6)$$

If the dependence of $D_i(\delta)$, $F_i(\delta)$, and $H_i(\delta)$ upon δ is small, they can be simply approximated as follows:

$$D_i(\delta)\approx D_0(1+k_d\delta), \qquad (7)$$

$$F_i(\delta)\approx F_0(1+k_f\delta), \qquad (8)$$

$$H_i(\delta)\approx H_0(1+k_h\delta). \qquad (9)$$

Here D_0, F_0, and H_0 are intrinsic nonlinear coefficients that have the following relationships with the nonlinear optical parameters [their physical implications are the same as those of D, F, and H in Eq. (1)]:

$$D_0=1/|M|^2\sum_{ij}(X_{ii}X_{jj}+2M_iY_{ijj}), \qquad (10)$$

$$F_0=\frac{1}{2}\mathrm{Tr}(\Delta\boldsymbol{\alpha})+(2/|M|^2)\left(\sum_{ij}M_iX_{ij}\right)\Delta\boldsymbol{\mu}, \qquad (11)$$

$$H_0=|\Delta\boldsymbol{\mu}|^2. \qquad (12)$$

Inserting Eq. (7) into Eq. (6), the first term of Eq. (6) takes the following form,

$$\int d\delta\rho(\delta)\frac{1}{3}D_i(\delta)A_0(\nu-\nu_0-\delta)$$
$$=\frac{1}{3}D_0\int d\delta\rho(\delta)A_0(\nu-\nu_0-\delta)$$
$$+\frac{1}{3}D_0k_d\int d\delta\delta\rho(\delta)A_0(\nu-\nu_0-\delta)$$
$$=\frac{1}{3}D_0A(\nu)+\frac{1}{3}D_0k_d\int d\delta\delta\rho(\delta)A_0(\nu-\nu_0-\delta). \qquad (13)$$

In the same way, the second and the third terms of Eq. (6) are written as

$$\int d\delta\rho(\delta)\frac{1}{3}F_i(\delta)\nu\frac{d[A_0(\nu-\nu_0-\delta)/\nu]}{hd\nu}$$
$$=\frac{1}{3}F_0A(\nu)\nu\frac{d[A(\nu)/\nu]}{hd\nu}$$
$$+\frac{1}{3}F_0k_f\nu\frac{d}{hd\nu}\int d\delta\delta\rho(\delta)A_0(\nu-\nu_0-\delta)/\nu, \qquad (14)$$

and

$$\int d\delta\rho(\delta)\frac{1}{3}H_i(\delta)\nu\frac{d^2[A_0(\nu-\nu_0-\delta)/\nu]}{2h^2d\nu^2}$$

$$=\frac{1}{3}H_0\nu\frac{d^2[A(\nu)/\nu]}{2h^2d\nu^2}$$

$$+\frac{1}{3}H_0k_h\nu\frac{d^2}{2h^2d\nu^2}\int d\delta\delta\rho(\delta)A_0(\nu-\nu_0-\delta)/\nu.$$

$$(15)$$

In order to describe the second terms of Eqs. (13), (14), and (15) as the first-, second-, and third-order derivatives of $A(\nu)$, respectively, the following three assumptions were applied.

(1) The homogeneous band A_0 has a Lorentz functional shape.

(2) The distribution function $\rho(\delta)$ is a normalized Gaussian function with inhomogeneous bandwidth σ_i based on the same assumption adopted by Krawczyk and Olszówka for carotenoids.[14] To use the Gaussian function is supported by the theoretical consideration by Frank-Kamenetskii and Lukashin.[24] $\rho(\delta)$ can then be described as

$$\rho(\delta)=\frac{1}{\sqrt{\pi}\sigma_i}\exp\left[-\left(\frac{\delta}{\sigma_i}\right)^2\right].$$

(3) The peak frequency of the absorption band is much larger than its bandwidth. The following approximation can thus hold:

$$\frac{dA(\nu)}{d\nu}\approx\nu\frac{d[A(\nu)/\nu]}{d\nu}.$$

On the basis of these assumptions, the second terms of Eqs. (13)–(15) can be expressed as

$$\frac{1}{3}D_0k_d\int d\delta\delta\rho(\delta)A_0(\nu-\nu_0-\delta)$$

$$=-\frac{1}{6}D_0k_d\sigma_i^2\int d\delta\frac{d\rho}{d\delta}A_0(\nu-\nu_0-\delta)$$

$$=-\frac{1}{6}D_0k_d\sigma_i^2\frac{dA(\nu)}{d\nu}\approx-\frac{1}{6}D_0k_d\sigma_i^2\nu\frac{d[A(\nu)/\nu]}{d\nu},$$

$$(16)$$

$$\frac{1}{3}F_0k_f\nu\frac{d}{hd\nu}\int d\delta\delta\rho(\delta)A_0(\nu-\nu_0-\delta)/\nu$$

$$\approx-\frac{1}{6}F_0k_f\sigma_i^2\nu\frac{d^2[A(\nu)/\nu]}{hd\nu^2},$$

$$(17)$$

$$\frac{1}{3}H_0k_h\nu\frac{d^2}{2h^2d\nu^2}\int d\delta\delta\rho(\delta)A_0(\nu-\nu_0-\delta)/\nu$$

$$\approx-\frac{1}{6}H_0k_h\sigma_i^2\nu\frac{d^3[A(\nu)/\nu]}{2h^2d\nu^3}.$$

$$(18)$$

When the homogenous bandwidth is much narrower than the inhomogeneous bandwidth σ_i, the absorption bandwidth Σ is approximately equal to σ_i. The EA spectrum can be finally described as the following formulation:

$$\Delta A(\nu)=\frac{1}{3}\left[D_0A(\nu)+\left(F_0-\frac{1}{2}D_0k_dh\Sigma^2\right)\nu\frac{d[A(\nu)/\nu]}{hd\nu}\right.$$

$$\left.+(H_0-F_0k_fh\Sigma^2)\nu\frac{d^2[A(\nu)/\nu]}{2h^2d\nu^2}\right]E_{int}^2.\quad(19)$$

Here the third-order derivative term of the absorption spectrum is neglected. According to Eq. (19), nonlinear coefficients (D, F, and H) have the following relationships with the intrinsic nonlinear optical coefficients and bandwidth:

$$D=D_0,\quad(20)$$

$$F=F_0-\tfrac{1}{2}k_dhD_0\Sigma^2,\quad(21)$$

$$H=H_0-k_fhF_0\Sigma^2.\quad(22)$$

These relationships reveal two remarkable features; first that the D value is equal to D_0, thus the transition dipole-moment polarizability and its hyperpolarizability can be directly evaluated from this term; second there is a square Σ term in F and H values in addition to the F_0 and H_0 terms. Thus $\Delta\alpha$ and $\Delta\mu$ values cannot be directly derived from the F and H values if inhomogeneous band broadening affects nonlinearity.

C. Physical implications of nonlinear optical parameters of HE band

Equation (22) indicates that if inhomogeneous band broadening affects nonlinearity, the H term can assume a negative value. Negative H values in the HE band imply the presence of that effect. Thus, in order to correctly determine $\Delta\alpha$ and $\Delta\mu$ values of the HE band, it is necessary to evaluate F_0 and H_0 values in F and H. Since the F_0 and H_0 values cannot be directly derived from the F and H values, theoretical estimate was performed of the $\Delta\alpha$ and $\Delta\mu$ values with semiempirical theoretical calculations.

1. The difference of charge distribution between HOMO and LUMO+1

Since the radius of charge distribution affects polarizability α,[25] a change in the charge distribution upon photoexcitation will reveal the characteristics of $\Delta\alpha$. The difference was estimated of charge distribution between HOMO and LUMO+1 states with INDO/CI molecular-orbital calculation for the evaluation of $\Delta\alpha$ of the HE band. Figures 4(a) and 4(b) indicate the charge distribution of HOMO state and
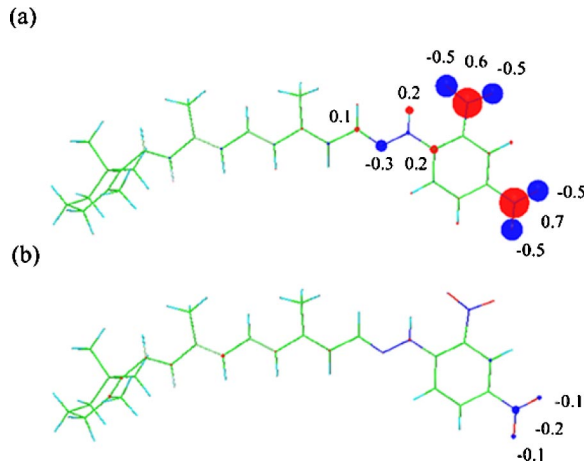
FIG. 4. (Color online) (a) The charge distribution of HOMO state and (b) the difference of charge distribution between HOMO and LUMO+1 states in C20-DNPH calculated by the INDO/CI method. Filled blue and red circles indicate net negative and positive charges on the atoms. The numbers indicate their quantities on largely charged atoms. The charge difference upon photoexcitation takes place mainly at the nitro-oxide group of the *para* position.

the difference of charge distribution between HOMO and LUMO+1 states in C20-DNPH, respectively. It shows that the charge difference upon photoexcitation takes place mainly at the nitro-oxide group of the *para* position. This fact indicates that the difference of polyene length does not affect the Δa value of the HE band.

2. Theoretical calculation of $\Delta\mu$ values of the HE bands

Theoretically calculated $\Delta\mu$ values ($\Delta\mu_{\text{theo}}$) were derived for HE bands of the hydrazones with the INDO/CI calculation. The results are shown in Table II and indicates that the HE bands of the hydrazones take a constant $\Delta\mu_{\text{theo}}$ value.

Table I and the preceding theoretical calculations indicate that D_0, F_0, and H_0 of the HE band have their own constant values regardless of any polyene length difference between the hydrazones. Therefore, according to Eqs. (20)–(22), change of the F and H values in the HE bands of the hydrazones reflects the difference of the bandwidth Σ. On the basis of these equations, values for F_0 and H_0 were determined from the dependence of F and H values on the bandwidth.

Figure 5 shows the dependence of the F values on $D_0\Sigma^2$. According to Eq. (21), an F_0 value of -1.3×10^{-37} (C m^2/V) could be derived from the linear dependence of F on $D_0\Sigma^2$. Figure 6 shows the dependence of the H values on $F_0\Sigma^2$. According to Eq. (22), an H_0 value of 3.3×10^{-57} (C m)^2 could be derived from the linear dependence of H on $F_0\Sigma^2$. Finally, the underlying $\Delta\mu$ value of the

TABLE II. Theoretically calculated $\Delta\mu$ values of the hydrazone HE bands.

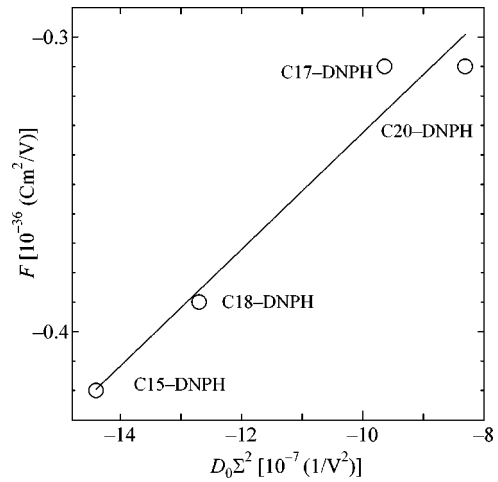|	C15-DNPH	C18-DNPH	C17-DNPH	C20-DNPH
$\Delta\mu_{\text{theo}}$ [D]	14.1	13.5	13.3	12.7

FIG. 5. The dependence of the F values on $D_0\Sigma^2$. The circles are experimentally determined F values of the hydrazones. F values have linear dependence on $D_0\Sigma^2$.

HE band was determined as 17 [D] from the derived H_0 value.

The above analysis based on the results shown in Figs. 5 and 6 implicitly supposes the linear dependence of F and H values on Σ^2. On the other hand, it can be pointed out that there is a significant deviation from the linear dependence in some data points. The linear dependence was derived by the theoretical consideration shown in Eqs. (21) and (22). Here we assumed that the D_0, F_0, and H_0 had their own constant values among C15 ~ C20-DNPH. If this assumption was not valid, some deviations from the linear dependence could naturally take place. However, the validity of this particular assumption still can be supported by the fact that thus determined underlying $\Delta\mu$ value is thought to be very reasonable because of the following reasons. (1) It agrees well with the $\Delta\mu_{\text{theo}}$ values, and (2) it is consistent with the reported $\Delta\mu$ values (10~40 [D]) in nonsymmetrical carotenoids.[9,26] Therefore, it was concluded that even if inhomogeneous band broadening affects nonlinearity, the underlying $\Delta\mu$
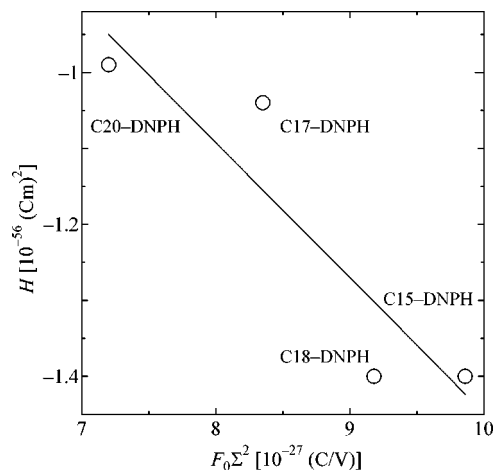

FIG. 6. The dependence of the H values on $F_0\Sigma^2$. The circles are experimentally determined H values of the hydrazones. H values have linear dependence on $F_0\Sigma^2$.

value could be properly deduced from the dependence of F and H values on the bandwidth.

IV. CONCLUSION

In this study we have derived a generalized formulation about the effect of inhomogeneous band broadening on nonlinearity. This derived formulation has revealed two remarkable features: (1) the transition dipole-moment polarizability and its hyperpolarizability can be directly evaluated from the D term regardless of the presence of the effect of inhomogeneous band broadening upon nonlinearity: (2) $\Delta\alpha$ and $\Delta\mu$ values cannot be directly estimated from the F and the H terms when the inhomogeneous band broadening affects nonlinearity. On the basis of our formula, we analyzed the EA spectra of a series of hydrazones derived from biological polyenes. Although $\Delta\mu$ value of the hydrazones could not be directly estimated from the H values due to the inhomogeneous band broadening effect, it could be derived from the dependence of the F and the H values on bandwidth.

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