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# Measurement of the depolarization ratio of Rayleigh scattering at absorption bands

J. Anglister and I. Z. Steinberg

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Measurements of the depolarization ratio  $\rho_v$  of light scattered by the pigments lycopene and  $\beta$ -carotene at the red part of their absorption bands yielded values which are very close to the theoretical value  $1/3$  of a fully anisotropic molecular polarizability, i.e., that due to an electric dipole moment. Measurements of  $\rho_v$  at the blue edge of the visible absorption band of pinacyanol chloride yielded a value of 0.75 at 472.2 nm, which is the maximum value that a depolarization ratio can assume, and is attained if the average molecular polarizability is zero. This is possible only if the diagonalized polarizability tensor has at least one negative element to counterbalance the positive ones. A negative refractive index at the blue edge of the absorption band is thus experimentally demonstrated.

## INTRODUCTION

Rayleigh light scattering by molecules at their absorption bands is significantly stronger than that at the spectral range at which they do not absorb.<sup>1,2</sup> This is due both to the enhancement of the real part of the refractive index, and the emergence of an imaginary component in the refractive index, as one approaches the spectral range of light absorption. The contribution of the solute to the Rayleigh ratio of the medium is given by

$$R_{v,v_H}(90^\circ) = \frac{4000\pi^2 \bar{n}^2 C}{\lambda_0^4 N_A} \left[ \left( \frac{\partial n}{\partial C} \right)^2 + \left( \frac{\partial k}{\partial C} \right)^2 \right] \cdot C_v \quad (1)$$

$R_{v,v_H}$  is the Rayleigh ratio for vertically polarized incident beam and total scattered light at  $90^\circ$  regardless of polarization,  $\bar{n}$  is the refractive index of the medium,  $\partial n/\partial C$  and  $\partial k/\partial C$  are, respectively, the increments (per 1 M solute concentration) in the real and imaginary components of the refractive index of the solution due to the scattering particles,  $N_A$  is Avogadro's number,  $C$  is the molarity of the solution, and  $C_v$  is the Cabannes factor which accounts for the enhancement of the intensity of the scattered light when it is depolarized<sup>2,3</sup> [ $C_v = (6 + 6\rho_v)/(6 - 8\rho_v)$ , where  $\rho_v$  is the depolarization ratio]. The imaginary part  $k$  of the refractive index is related exclusively to the quantum transition which is responsible to the absorption band under consideration and is given by

$$k = 2.303 \epsilon C \lambda_0 / 4\pi \quad (2)$$

where  $\epsilon$  is the molar extinction coefficient and  $\lambda_0$  is the light wavelength. The real part is related to the whole absorption spectrum of the molecule by the Kramig-Kramers relationship

$$n = n_0 - \frac{2.303 C \lambda_0^2}{2\pi^2} \int_0^\infty \frac{\epsilon(\lambda)}{\lambda^2 - \lambda_0^2} d\lambda \quad (3)$$

where  $n$  is the refractive index of the solution and  $n_0$  is the refractive index of the pure solvent. It may be noted that the contribution of remote absorption bands in this relationship falls off steeply as their frequency diverges from the frequency under discussion, and at any given wavelength the contribution of the absorption band overlapping this wavelength to the real part of the refractive index is dominant, especially so if the absorption band

is an intense one. It therefore follows that the light scattering at an absorption band is dominated in its properties by the electronic transition of this band. It may be noted that depolarization of light scattered by anisotropic molecules was studied before both in the gas phase<sup>4</sup> and in solution,<sup>5</sup> but these studies were not performed within absorption bands.

In view of the above, the polarizability of a molecule at an absorption band which is electronically dipolar will be highly anisotropic. Let  $\alpha_1$ ,  $\alpha_2$ , and  $\alpha_3$  be the molecular polarizabilities along the principal polarizability axes of the molecule, and let  $\alpha_1$  be in the direction of the dipole transition moment of the relevant absorption band. The imaginary part of  $\alpha_1$  will be positive throughout, whereas its real part will be positive at the red edge of the absorption band and negative at the blue edge, and its absolute value at the extrema will be much larger than that of  $\alpha_2$  and  $\alpha_3$ , which draw contributions only from remote bands. This has interesting consequences as to the depolarization ratio of the scattered light, which is given for scattering at  $90^\circ$  to plane polarized incident light by  $\rho_v(90^\circ)$ :

$$\rho_v(90^\circ) = \frac{(3/45)\gamma^2}{(\bar{\alpha})^2 + (4/45)\gamma^2} \quad (4)$$

where  $\gamma$ , the molecular anisotropy factor, is defined by

$$\gamma^2 = \alpha_1^2 + \alpha_2^2 + \alpha_3^2 - \alpha_1\alpha_2 - \alpha_2\alpha_3 - \alpha_3\alpha_1 \quad (5)$$

and

$$\bar{\alpha} = (\alpha_1 + \alpha_2 + \alpha_3)/3 \quad (6)$$

For a pure dipolar transition the imaginary parts of  $\alpha_2$  and  $\alpha_3$  are zero. On the red part of the absorption band the relation  $\alpha_1 > \alpha_2, \alpha_3$  holds for real part of  $\alpha$ ;  $\rho_v$  is thus expected to be very nearly  $1/3$ . On the other hand, at the blue edge of the absorption band the real part of  $\alpha_1$  assumes a negative value, which may make  $\rho_v(90^\circ)$  assume a wide range of values, either smaller or greater than  $1/3$ , depending on the numerical values of the components of  $\alpha$ , the upper limit being as high as  $3/4$ , when  $\bar{\alpha}$  vanishes.

In the following we describe an experimental study of the value of  $\rho_v(90^\circ)$  for two pigments and one dye, at their absorption bands. In addition to its intrinsic interest, being related to the dipolar character of the

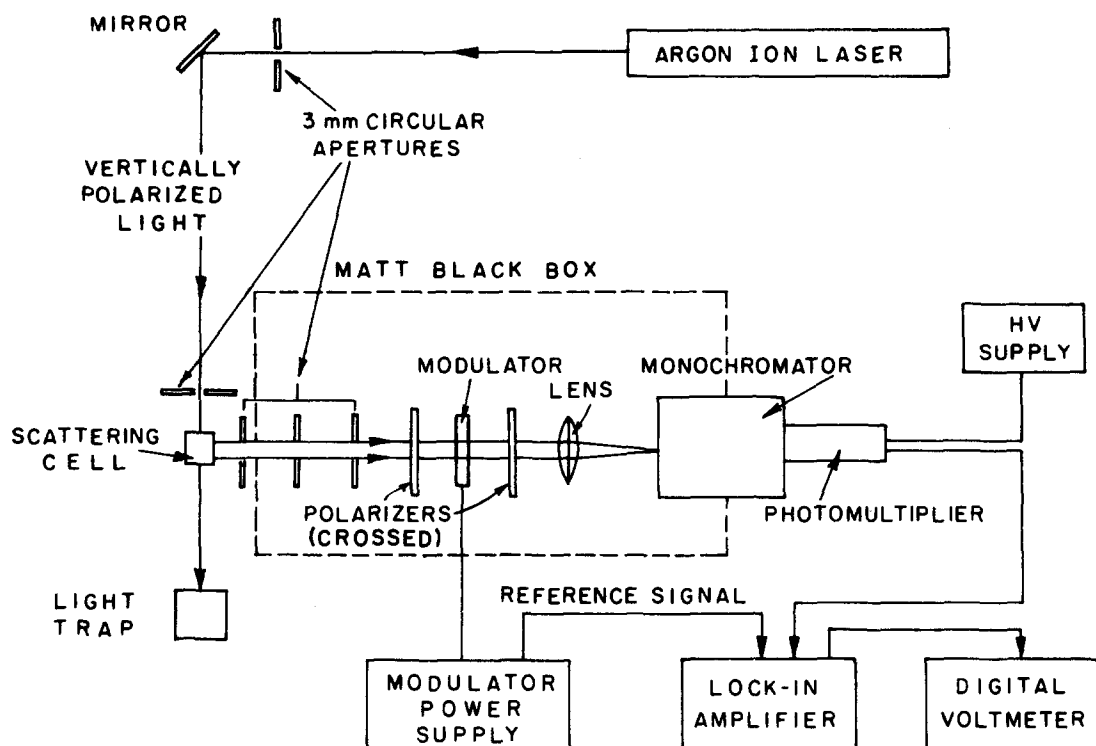


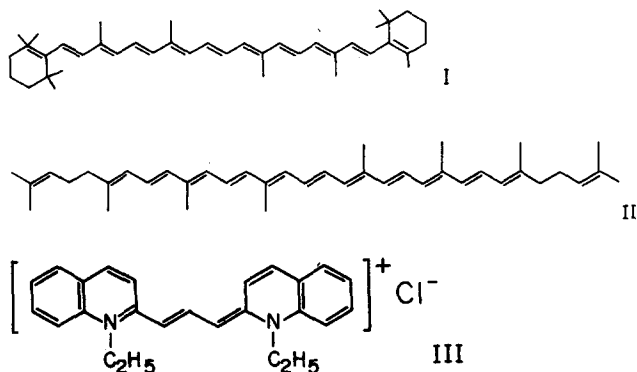
FIG. 1. Block diagram of the instrument used for the measurement of the depolarization ratio of the scattered light.

transition under discussion, a knowledge of  $\rho_v(90^\circ)$  is necessary for the evaluation of the light scattering intensity of chromophores at their absorption bands through the Cabannes factor.<sup>2,3</sup> Furthermore, for experimental reasons the measurement of depolarized light scattering by chromophores is more feasible than the measurement of the polarized or total scattering; a knowledge of  $\rho_v$  is therefore necessary for the interpretation of the experimental data.<sup>2</sup>

## EXPERIMENTAL

### Materials

$\beta$ -Carotene (I), of purity better than 95%, was a Koch-Light product, and was crystallized by us from petrol ether; Lycopene (II) (all *trans*) was prepared from tomato paste devoid of artificial coloring material, by the method of Davis<sup>6</sup>; pinacyanol chloride (III), of purity better than 98%, was an Eastman product and was crystallized by us from 90% ethanol in water:



All solvents used were of spectrograde quality (Fluka). Nitrogen (filtered through millipore of  $0.22 \mu$ ) was bubbled through the solvents for about 15 min before the preparation of the solutions.

### Light scattering instrument

A block diagram of the instrument is presented in Fig. 1. The light source is an argon-ion laser (Spectra Physics 164-09) which has ten lasing lines in the visible with linear polarization better than 50:1. The scattered light was collected at  $90^\circ$  to the plane of polarization and to the direction of propagation of the incident beam, and was modulated by an elasto-optic modulator (Hinds PEM-3) equipped with two Glan-Thomson polarizers (of extinction ratio better than  $10^{-5}$ ). The orientation of the polarizer in front of the elasto-optic element selects the polarization component of the scattered light. Following the modulator there is a monochromator (Jarrel-Ash 82-410), set to a bandwidth of 3.2 nm, and the light is detected by a photomultiplier (EM1 9789) cooled to  $2^\circ\text{C}$ . The signal is amplified by a phase-sensitive amplifier (Ithaco, Dynatrac 391-A). Readings were corrected for the different efficiency of the monochromator and photomultiplier to light of different polarization. Three circular apertures of 3 mm in diameter, spaced about 6 cm apart, were placed in the path of the viewing optics in order to limit the size of the acceptance angle, since large acceptance angles interfere with measurement of small depolarization ratios.<sup>7</sup> The modulation technique reduces stray light to a negligible level; only stray light which propagates in the direction of the viewing optics may interfere with the measurement. In order to avoid such stray light, that part of the optical system which collects the scattered light is placed in a matte-black

box, whereas the scattering cell is placed outside the box. The scattered light enters the box through a hole of 3 mm in diameter. The incident laser beam is directed to pass as closely as possible to the side of the cell in front of the viewing optics, which is aligned so as to collect the scattered light as closely as possible to the side of the cell on which the laser light impinges. Thus, the intensity of the scattered light which is collected is maximized. However, care was taken not to approach too close to the cell walls in order to avoid reflections from them or from the cell holder.

To reduce local heating of the solutions due to light absorption, and subsequent turbulence, the measurements were performed as fast as possible (in less than 1 min). The spectrophotometric cells used in the scattering experiments were cleaned according to the procedure of Dubin *et al.*<sup>8</sup>

### Analysis of measurements

Due to light absorption by the solute the practical magnitude of its concentration is limited, and the intensity of the light scattered by the dissolved pigments is appreciably lower (by 1 to 2 orders of magnitude) than that of the solvent. On the other hand, if one uses solvents which have a relatively low depolarization ratio  $\rho_{v,st}$  (e.g., cyclohexane was measured to have  $\rho_{v,st} = 0.0175 \pm 0.0005$  in the spectral range 454–515 nm; the value obtained by Pierens<sup>9</sup> is 0.0188 at 441 nm) the value of  $\rho_{v,sn}$  of the solution increases considerably on increasing the concentration of the dissolved pigment, due to the intrinsic high  $\rho_{v,dye}$  value of the pigment. Obviously, the change of  $\rho_{v,sn}$  with solute concentration contains information about  $\rho_{v,dye}$ . This information was extracted from the data as follows (note that the correct depolarization ratio is obtained by measurement of the pairs of intensities at orthogonal polarization directions regardless of some absorption of scattered light by the solution, since the solution is isotropic):

$$\rho_{v,sn} = \frac{C \cdot I_{\perp,dye} + I_{\perp,st}}{C \cdot I_{\parallel,dye} + I_{\parallel,st}}, \quad (7)$$

where  $C$  is the solute molar concentration;  $I_{\parallel,dye}$  and  $I_{\perp,dye}$  are, respectively, the intensities of the polarized and depolarized light scattered by the solute at unit concentration; and  $I_{\parallel,st}$  and  $I_{\perp,st}$  are, respectively, the intensities of polarized and depolarized light scattered by the solvent. The various intensities of scattering are defined per unit intensity of incident light. Our aim is to extract the value of  $\rho_{v,dye} = (I_{\perp,dye})/(I_{\parallel,dye})$  from a series of measurements of  $\rho_{v,sn}$  vs  $C$ . This is done by a series of reiterations. In the first step of the reiteration procedure neglect  $I_{\perp,st}$  in Eq. (7) to yield

$$\frac{C}{\rho_{v,sn}} = \frac{C}{\rho_{v,dye}} + \frac{I_{\parallel,st}}{I_{\perp,dye}}. \quad (8)$$

The slope of a plot of  $C/\rho_{v,sn}$  vs  $C$  yields the reciprocal of an unrefined value of  $\rho_{v,dye}$ , to be used in the next stage of the reiteration to correct for the neglected value of  $I_{\perp,st}$ . From Eq. (7) one obtains

$$\frac{I_{\perp,st}}{I_{\perp,dye}} = \frac{1 - \rho_{v,sn}/\rho_{v,dye}}{\rho_{v,sn}/\rho_{v,dye} - 1} = A. \quad (9)$$

$A$ , as defined by Eq. (9), can be approximately evaluated from the first-reiteration value of  $\rho_{v,dye}$ . In the subsequent reiterations we use the equation

$$\frac{C(1+A)}{\rho_{v,sn}} = \frac{C}{\rho_{v,dye}} + \frac{I_{\parallel,st}}{I_{\perp,dye}}; \quad (10)$$

the slope of the left hand side of this equation vs  $C$  yields a refined value for  $\rho_{v,dye}$ . This procedure is repeated until consecutive values of  $A$  and of  $\rho_{v,dye}$  converge. Usually, four steps sufficed. One can reduce the number of steps by using as a first guess a plausible value for  $\rho_{v,dye}$ , e.g., 0.30. It should be noted that the intercept of the plot of the left hand side of Eq. (10) vs  $C$

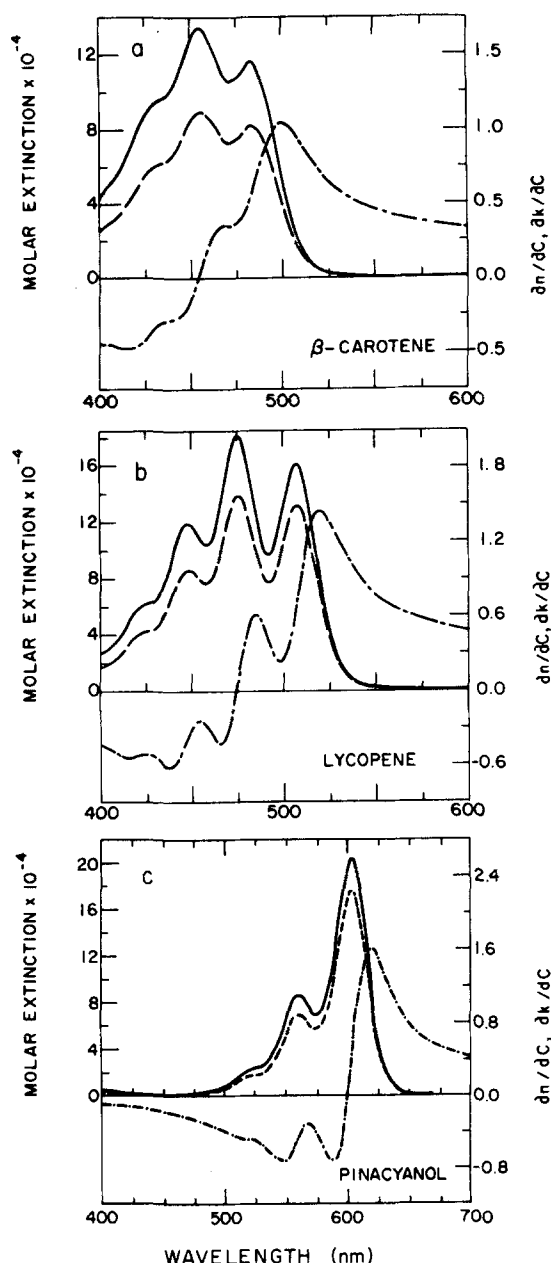


FIG. 2. Absorption spectra (—) and the calculated contribution of the solutes to the real (---) and imaginary (····) parts of the refractive index (per unit molar concentration)  $\delta n/\delta C$  and  $\delta k/\delta C$ , respectively. (a)  $\beta$ -carotene in cyclohexane; (b) lycopene in cyclohexane; (c) pinacyanol chloride in methanol.

with the  $y$  axis yields the absolute value of  $I_{L,dye}$  if the absolute value of  $I_{L,st}$  is known, thus permitting, in conjunction with  $\rho_{v,dye}$ , the evaluation of the Rayleigh ratio of the light scattered by the dye.

## RESULTS AND DISCUSSION

The spectral range of the measurements was restricted by the laser lines of the argon ion laser. The depolarization ratio of the two carotenoids studied ( $\beta$ -carotene and lycopene) was thus measured at the red shoulder of their absorption bands, whereas  $\rho_v$  of pinacyanol chloride was measured at the blue edge of its visible absorption band.

The absorption spectra of the three pigments studied are presented in Fig. 2. Also included in this figure are the partial specific real and imaginary components of the refractive index  $\partial n/\partial C$  and  $\partial k/\partial C$ , respectively, evaluated from the absorption spectra as described previously.<sup>1,2</sup>

### $\beta$ -Carotene

The depolarization ratio of the light scattered by  $\beta$ -carotene was measured in cyclohexane solution at three different wavelengths at the red part of its absorption band; 496.5, 501.7, and 514.5 nm. Plots of  $\rho_{v,sn}$  are presented in Fig. 3, and plots of the last reiteration of  $C(1+A)/\rho_{v,sn}$  (see "Experimental" section for details)

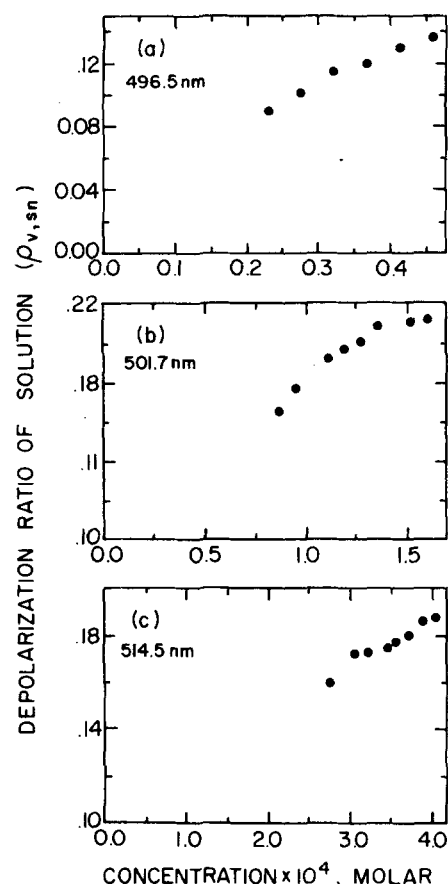


FIG. 3. The measured depolarization ratio of light scattered by  $\beta$ -carotene solutions in cyclohexane as a function of solute concentration. Light wavelength: (a) 496.5 nm; (b) 501.7 nm; (c) 514.5 nm.

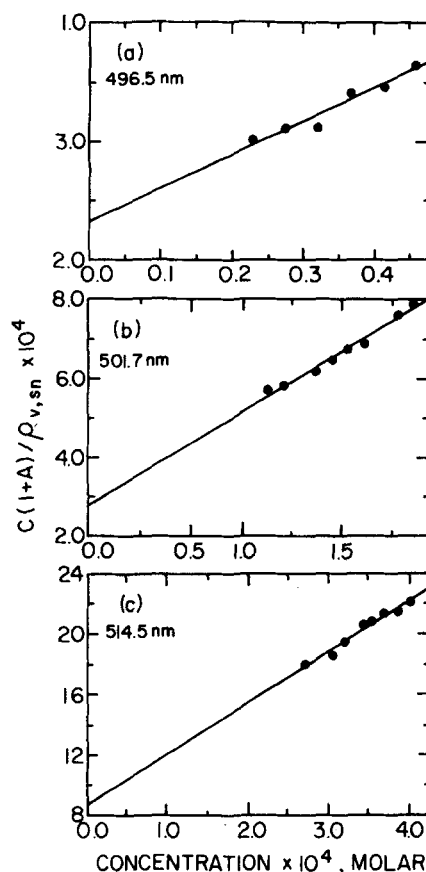


FIG. 4. Plots of the last reiteration of  $C(1+A)/\rho_{v,sn}$  as a function of  $\beta$ -carotene concentration in cyclohexane. The slope yields the reciprocal of the depolarization ratio of the pigment. Wavelength of scattered light: (a) 496.5 nm; (b) 501.7 nm; (c) 514.5 nm.

are presented in Fig. 4. From the slopes of the lines in Fig. 4 the values of  $\rho_{v,dye}$  were evaluated. From the intercepts of the above slopes with the  $y$  axis and the value of  $\rho_{v,st}$  of 0.0175 and  $R_{v,v,H}(90^\circ)$  for cyclohexane,<sup>10</sup> the molar Rayleigh ratios of  $\beta$ -carotene for depolarized scattering  $R_{v,H}^M(90^\circ)$  and for total (i.e., polarized plus depolarized) scattering  $R_{v,v,H}^M$  at  $90^\circ$  to the incident beam were calculated. The molar Rayleigh ratio is defined as the Rayleigh ratio divided by the corresponding molar concentration. The results are presented in Table I.

TABLE I. Depolarization ratio and Rayleigh ratio of light scattering by  $\beta$ -carotene in cyclohexane solution.

$\lambda(\text{nm})$	$\epsilon/\epsilon_{\text{max}}^a$	$\rho_{v,dye}$	$R_{v,H}^M(90^\circ) \times 10^{2b}$	$R_{v,v,H}^M(90^\circ) \times 10^{2c}$
496.5	0.52	$0.35 \pm 0.04$	$5.7 \pm 0.3$	$22 \pm 2$
501.7	0.33	$0.33 \pm 0.02$	$4.6 \pm 0.4$	$18 \pm 2$
514.5	0.066	$0.30 \pm 0.02$	$1.35 \pm 0.12$	$6.0 \pm 0.6$

<sup>a</sup> $\epsilon$  and  $\epsilon_{\text{max}}$  are the molar extinction coefficients at the wavelength under consideration and at the peak of the last absorption band, respectively.

<sup>b</sup> $R_{v,H}^M(90^\circ)$  is the molar Rayleigh ratio ( $\text{cm}^{-1}\text{M}^{-1}$ ) for vertically polarized incident light and horizontally polarized component of the scattered light.

<sup>c</sup> $R_{v,v,H}^M(90^\circ)$  is the molar Rayleigh ratio ( $\text{cm}^{-1}\text{M}^{-1}$ ) for vertically polarized incident light and scattered light regardless of polarization.

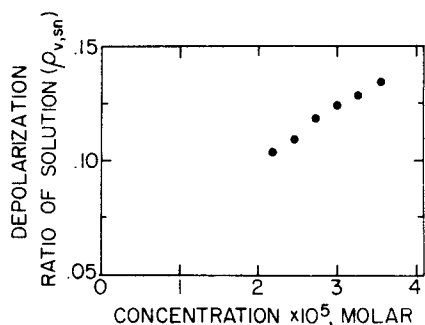


FIG. 5. The measured depolarization ratio of light scattered by lycopene solution in cyclohexane as a function of solute concentration. Light wavelength: 514.5 nm.

As seen from Table I, the value of  $\rho_{v,dye}$  at the red edge of the absorption band of  $\beta$ -carotene is very close to the theoretical value of  $1/3$  expected for an extremely anisotropic molecule for which two of the three diagonalized elements of the anisotropy tensor vanish, i.e.,  $\alpha_2 = \alpha_3 = 0$ . This is an experimental correlate of the electric dipolar character to be expected for the intense transition under consideration.

### Lycopene

The depolarization ratio of the light scattered by lycopene was measured at 514.5 nm, which is at the red part of its absorption band. A plot of  $\rho_{v,sn}$  for this wavelength is presented in Fig. 5, whereas a plot of the last reiteration of  $C(1+A)\rho_{v,sn}$  vs  $C$  is given in Fig. 6. From the inverse of the slope of the latter plot,  $\rho_{v,dye}$  was found to be  $0.30 \pm 0.02$ . This is quite close to the value of  $1/3$  expected for the electric dipolar transition of the absorption band under consideration. The somewhat lower value obtained experimentally for  $\rho_{v,dye}$  is probably due to the finite, though relatively low, contribution of remote absorption bands to the refractive index in directions that are different from the one to which the last absorption band contributes.

From the intercept on the  $y$  axis of the plot presented in Fig. 6 the values of  $R_{v,H}^M(90^\circ)$  and  $R_{v,v+H}^M(90^\circ)$  of lycopene were found to be  $6.96 \times 10^{-2}$  and  $0.301 \text{ cm}^{-1} \text{ M}^{-1}$ , respectively. These values are in agreement with the

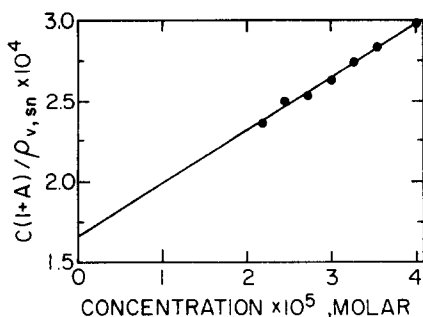


FIG. 6. A plot of the last reiteration of  $C(1+A)/\rho_{v,sn}$  as a function of lycopene concentration in cyclohexane. The slope yields the reciprocal of the depolarization ratio of the pigment. Wavelength of scattered light: 514.5 nm.

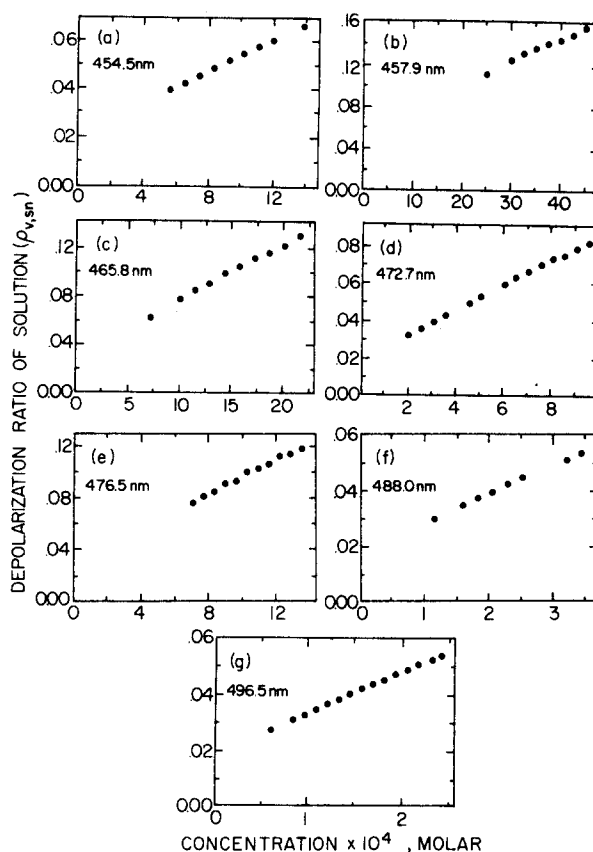


FIG. 7. The measured depolarization ratio of light scattered by pinacyanol chloride solutions in methanol as a function of solute concentration. Light wavelength: (a) 454.5 nm; (b) 457.9 nm; (c) 465.8 nm; (d) 472.7 nm; (e) 476.5 nm; (f) 488.0 nm; (g) 496.5 nm.

Rayleigh ratios  $R_{v,v+H}(90^\circ)$ , measured directly [Anglister and Steinberg (in preparation)].

### Pinacyanol chloride

In contrast to the two pigments discussed above, the depolarization ratio of the light scattered by pinacyanol chloride was measured at the blue edge of its visible absorption band, at the wavelengths 454.5, 457.9, 465.8, 472.7, 476.5, 488.0, and 496.5 nm. The solvent was methanol whose  $\rho_v$  was found to be  $0.0171 \pm 0.0005$ . Measurements on the blue edge of the absorption band of pinacyanol were more difficult than those reported above for the red edge of the  $\beta$ -carotene and lycopene bands, because of the lower value of  $R_{v,H}^M(90^\circ)/\epsilon$  found for the pinacyanol solutions above 475 nm.

The results for  $\rho_{v,dye}$  for various concentrations of pinacyanol chloride are presented in Fig. 7. Corresponding plots for the final reiteration of  $C(1+A)/\rho_{v,sn}$  vs  $C$  are presented in Fig. 8. The values of  $\rho_{v,dye}$ ,  $R_{v,H}^M(90^\circ)$ , and  $R_{v,H+V}^M(90^\circ)$  for pinacyanol chloride deduced from Fig. 8 and from  $R_{v,v+H}(90^\circ)$  of methanol<sup>11</sup> are presented in Table II.

As can be seen from Table II, in the case of pinacyanol,  $\rho_{v,dye}$  varies with wavelength in a very interesting way. At 472.7 nm it reaches its highest value, i.e., 0.75, which is the maximum value possible theoretically

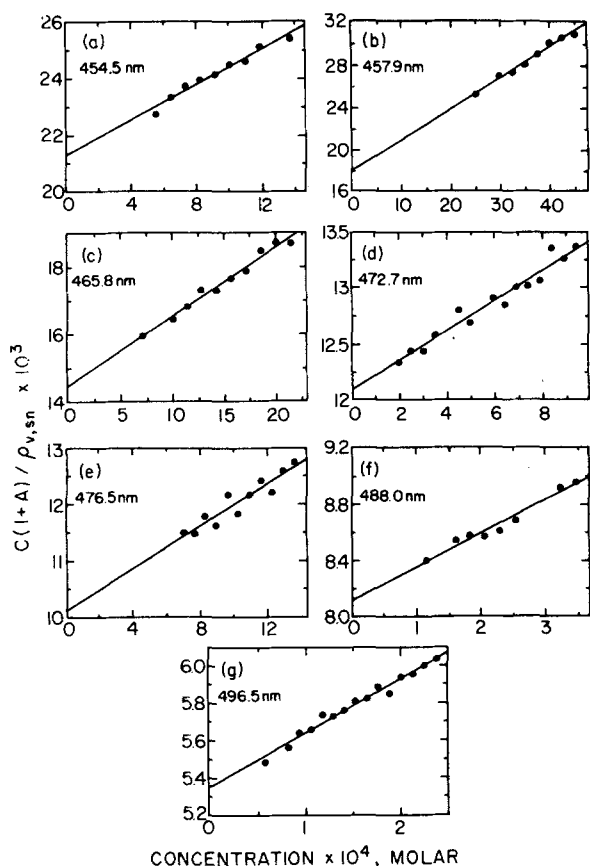


FIG. 8. Plots of the last reiteration of  $C(1+A)/\rho_{v,sn}$  as a function of pinacyanol chloride concentration in methanol. The slope yields the reciprocal of the depolarization ratio of the dye. Wavelength of scattered light: (a) 454.5 nm; (b) 457.9 nm; (c) 465.8 nm; (d) 472.7 nm; (e) 476.5 nm; (f) 488.0 nm; (g) 496.5 nm.

(for the special case for which  $\bar{\alpha} = 0$ ). This means that at this wavelength the negative value of  $\alpha_1$  is just of the right magnitude to balance  $\alpha_2 + \alpha_3$  so that the values of  $\bar{\alpha}$  vanishes. As one approaches the center of the absorption band the value of  $\rho_{v,dye}$  tends towards  $1/3$ . At the center of the band the scattering is dominated by the contribution of the out-of-phase polarizability, which will make  $\rho_{v,dye} = 1/3$  for a dipolar transition (see "Introduction"). The drop in the value of  $\rho_{v,dye}$  on the blue side of 472.7 nm is understandable but cannot be discussed quantitatively, since contributions from additional absorption bands become significant, the data about which are not available.

It should be remembered that the solute molecules in the experiments reported are not in vacuum but are embedded in a medium, and most probably interact with the solvent molecules in a nonisotropic fashion. The latter, which are nonisotropic, are thus organized along the solute molecules and contribute to both the intensity of scattering and its depolarization. This is automatically taken care of in Eq. (1) by using the partial specific quantities  $\partial n/\partial C$  and  $\partial k/\partial C$ .

The anisotropy of light absorption by chromophores has been studied by linear dichroism of the chromophores embedded in stretched films, e.g., of polyethylene or polyvinyl alcohol. By this method the transition

TABLE II. Depolarization ratio and Rayleigh ratio of light scattering by pinacyanol chloride in methanol solution.

$\lambda$ (nm)	$\epsilon/\epsilon_{\max}^a$	$\rho_v$	$R_{v,H}^M(90^\circ) \times 10^{14}{}^b$	$R_{v,v+H}^M(90^\circ) \times 10^{13}{}^c$
454.5	0.0033	$0.32 \pm 0.02$	$4.70 \pm 0.05$	$1.93 \pm 0.15$
457.9	0.0038	$0.35 \pm 0.03$	$5.6 \pm 0.2$	$2.2 \pm 0.3$
465.8	0.0058	$0.49 \pm 0.025$	$6.27 \pm 0.07$	$1.91 \pm 0.15$
472.7	0.0092	$0.75 \pm 0.05$	$7.08 \pm 0.03$	$1.65 \pm 0.15$
476.5	0.0122	$0.51 \pm 0.06$	$8.2 \pm 0.2$	$2.4 \pm 0.4$
488.0	0.022	$0.40 \pm 0.03$	$9.28 \pm 0.06$	$3.2 \pm 0.35$
496.5	0.031	$0.340 \pm 0.015$	$13.2 \pm 0.1$	$5.2 \pm 0.3$

<sup>a</sup> $\epsilon$  and  $\epsilon_{\max}$  are the molar extinction coefficients at the wavelength under consideration and at the peak of the last absorption band, respectively.

<sup>b</sup> $R_{v,H}^M(90^\circ)$  is the molar Rayleigh ratio ( $\text{cm}^{-1} \text{M}^{-1}$ ) for vertically polarized incident light and horizontally polarized component of the scattered light.

<sup>c</sup> $R_{v,v+H}^M(90^\circ)$  is the molar Rayleigh ratio ( $\text{cm}^{-1} \text{M}^{-1}$ ) for vertically polarized incident light and scattered light regardless of polarization.

dipole moment of the last absorption band of  $\beta$ -carotene<sup>12</sup> and pinacyanol<sup>13</sup> were shown to be oriented along the molecular long axis. However, perfect orientation of the chromophores is difficult to obtain, and therefore the degree of dichroism observed was not 100%. It is thus difficult to demonstrate by this method that a transition is fully anisotropic. The polarization of fluorescence light is another measurement that involves the anisotropy of light absorption, but involves also the anisotropy of emission. Therefore, useful as fluorescence polarization is for a variety of purposes, it is not as straightforward as light scattering for the study of the degree of polarization of light absorption by a chromophore. None of the above methods can be applied to the measurement of the anisotropy of the real component of the refractive index of a solute (in stretched films the contribution of the solute will be completely masked by the embedding medium). The results obtained by depolarized light scattering of pinacyanol demonstrating the negative refractive index at the blue part of the visible absorption band may thus be considered as quite unique to the light scattering measurements.

<sup>1</sup>G. A. Miller, J. Phys. Chem. 82, 616 (1978).

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