

Effect of macromolecular length on anisotropic scattering of light in an electric field*

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(Received 9 April 1976)

Light scattering by monodisperse solutions of rigid rod-like anisotropic macromolecules, with linear dimensions l of the order of incident wavelength λ , oriented in an external d.c. electric field, \vec{E} has been analysed. The relative variations δV_v^E , δH_v^E , δV_h^E , δH_h^E of the scattered light components are discussed for the three values $[l/\lambda] = 1, 0.5, 2$, and various reorientation parameters, $p = [\mu E/kT]$ of the permanent dipole moment μ and $q = [(\alpha_3 - \alpha_1)E^2/2kT]$ of the moment induced by the principal polarizabilities $\alpha_1 = \alpha_2 \neq \alpha_3$. The saturation orientation field strength has been calculated for certain macromolecules with the aim of determining their optical anisotropy numerically.

INTRODUCTION

Relative intensity variations of the components of light scattered by monodisperse solutions of macromolecules, oriented in an external d.c. electric field, are a source of abundant data concerning their optical, electric and geometrical properties¹. The field effect has been considered for large macromolecules, of linear dimensions comparable with the incident light wavelength, for particular cases of the Rayleigh-Debye-Gans approximation^{2,3}. Wippler and Benoit⁴ analysed theoretically the influence of a d.c. electric field on the particle interference scattering factor, $P(\theta)$, with an accuracy to the square of the field strength E . Stoylov^{5,6} extended their analysis to intense fields, including electric saturation. Ravey⁷ gave a description of the effect of arbitrary orientations of macromolecules having the shape of spheres, rods, discs and Gaussian chains in a d.c. electric field, acting in the direction of the external bisector of the observation angle.

In the present study, on the basis of previous theory^{8,9}, we give an analysis of the relative variations δV_v^E , δH_v^E , δV_h^E and δH_h^E of the respective components of light scattered by solutions of large rod-like macromolecules, oriented by a d.c. electric field applied perpendicularly to the plane of observed scattered light. Our results are obtained by numerical computer calculation of the relative variations for the three values $[l/\lambda] = 1, 0.5$ and 2 , and for various values of the reorientation parameters of the permanent dipole moments and polarizability ellipsoids.

THEORY

Consider dilute, monodisperse solutions of rigid, aniso-

tropic, non-absorbing macromolecules in the shape of rods, of rotation-ellipsoidal symmetry. We have assumed that the symmetry axis of their electric and optical properties coincides with their geometrical axis. Thus, the principal electric polarizability, α_3 , and optical polarizability, a_3 , are parallel to the symmetry axis, the principal 3-axis of the macromolecule, whereas the principal polarizabilities $\alpha_1 = \alpha_2$ and $a_1 = a_2$ are perpendicular. The permanent dipole moment is also assumed to lie along the symmetry axis.

Relative variations in scattered light intensity can be defined as follows^{5,6}:

$$\delta I^E = \frac{I^E - I^0}{I^0} \quad (1)$$

where I^E and I^0 represent the intensity of light scattered in the presence and absence of the d.c. field \vec{E} . Considering the experimental arrangement shown in Figure 1, and taking into account equation (1) and the expression for I^E and I^0 proposed by Kielich⁹ and Horn², respectively, one can write the relative variations of the vertical (V) and horizontal (H) components of scattered light when the incident light beam is polarized vertically (v), or horizontally (h), as follows:

$$\delta V_v^E = \frac{1}{V_v^0} \times \frac{2\pi}{0} \frac{\pi}{0} [1 + 2\kappa(3 \cos^2 \nu - 1) + \kappa^2(9 \cos^4 \nu - 6 \cos^2 \nu + 1)] |R(\nu, \phi)|^2 \times \frac{\exp(p \cos \nu + q \cos^2 \nu) \sin \nu d\nu d\phi}{2\pi \int_0^\pi \exp(p \cos \nu + q \cos^2 \nu) \sin \nu d\nu} - 1 \quad (2)$$

* Reported in part at the International Symposium on Electro-optical Properties of Macromolecular Solutions, Liège, September 1974.

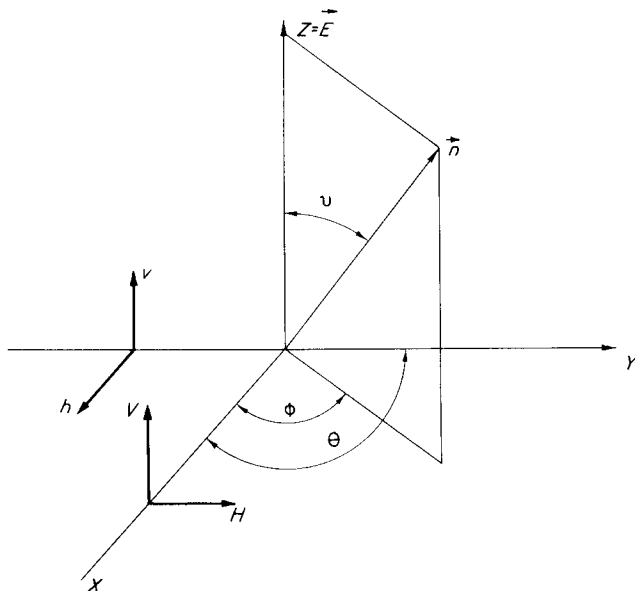


Figure 1 The light beam is incident in the Y -direction with its electric vector $\vec{E}(\omega)$ vibrating in the XZ -plane (the direction of the electric vector vibrations defines the light polarization direction: v , vertical; h horizontal). The scattered light is observed in the x -direction (observation angle $\Theta = 90^\circ$), with the vertical and horizontal component of scattered light denoted by V and H , respectively. θ is the angle between the Z -axis and the macromolecular symmetry axis \vec{n} , whereas ϕ is the azimuth of \vec{n} . The orienting electric field \vec{E} is directed along Z .

$$\delta V_h^E = \frac{1}{V_h^0} \times \frac{9\kappa^2 \int_0^{2\pi} \int_0^\pi \cos^2 \nu \sin^2 \nu \cos^2 \phi |R(\nu, \phi)|^2 \times \exp(p \cos \nu + q \cos^2 \nu) \sin \nu d\nu d\phi}{2\pi \int_0^\pi \exp(p \cos \nu + q \cos^2 \nu) \sin \nu d\nu} - 1 \quad (3)$$

$$\delta H_v^E = \frac{1}{H_v^0} \times \frac{9\kappa^2 \int_0^{2\pi} \int_0^\pi \cos^2 \nu \sin^2 \nu \sin^2 \phi |R(\nu, \phi)|^2 \times \exp(p \cos \nu + q \cos^2 \nu) \sin \nu d\nu d\phi}{2\pi \int_0^\pi \exp(p \cos \nu + q \cos^2 \nu) \sin \nu d\nu} - 1 \quad (4)$$

$$\delta H_h^E = \frac{1}{H_h^0} \times \frac{9\kappa^2 \int_0^{2\pi} \int_0^\pi \sin^4 \nu \cos^2 \phi \sin^2 \phi |R(\nu, \phi)|^2 \times \exp(p \cos \nu + q \cos^2 \nu) \sin \nu d\nu d\phi}{2\pi \int_0^\pi \exp(p \cos \nu + q \cos^2 \nu) \sin \nu d\nu} - 1 \quad (5)$$

where²:

$$V_v^0 = (1 - \kappa)^2 \left[\frac{Si(2K)}{K} - \left(\frac{\sin K}{K} \right)^2 \right] + 3\kappa(1 - \kappa) \left[\frac{Si(2K)}{K} + \frac{\sin 2K}{4K^3} - \frac{1}{K^2} + \frac{\cos 2K}{2K^2} \right] + \frac{27}{8} \kappa^2 \left[\frac{Si(2K)}{K} - \frac{4}{3K^2} - \frac{\cos 2K}{4K^4} - \frac{\sin 2K}{4K^3} + \frac{\cos 2K}{2K^2} + \frac{\sin 2K}{8K^5} \right] \quad (6)$$

$$V_h^0 = H_v^0 = 9\kappa^2 \left[\frac{Si(2K)}{16K} + \frac{\cos 2K}{32K^2} + \frac{\sin 2K}{64K^3} + \frac{3 \cos 2K}{64K^4} - \frac{3 \sin 2K}{128K^5} \right] \quad (7)$$

$$H_h^0 = 9\kappa^2 \left[\frac{3Si(2K)}{32K} - \frac{1}{6K^2} + \frac{3 \cos 2K}{64K^2} - \frac{5 \sin 2K}{128K^3} - \frac{19 \cos 2K}{128K^4} + \frac{19 \sin 2K}{256K^5} \right] \quad (8)$$

where,

$$\kappa = \frac{a_3 - a_1}{a_3 + 2a_1} \quad (9)$$

defines the optical anisotropy of the macromolecule, whereas

$$p = \frac{\mu E}{kT} \quad \text{and} \quad q = \frac{(\alpha_3 - \alpha_1)}{2kT} E^2 \quad (10)$$

are dimensionless reorientation parameters of the permanent dipole moment, μ , and electric polarizability ellipsoid; k is Boltzmann's constant and T the absolute temperature. For rod-like macromolecules, in the Rayleigh-Debye-Gans approximation, the function $R(\theta, \phi)$ is of the form³:

$$R(\theta, \phi) = \frac{\sin \left[K \sin \theta \cos \left(\phi + \frac{\Theta}{2} \right) \right]}{K \sin \theta \cos \left(\phi + \frac{\Theta}{2} \right)} \quad (11)$$

where $K = [(2\pi l \sin \Theta / 2) / \lambda]$ is a parameter dependent on the length l of the object, the observation angle, Θ and the wavelength, λ , of incident light.

DISCUSSION

In the case of small macromolecules, the component variations, equations (2)–(5) can be expressed in the variables p and q in terms of generalized Langevin functions⁹. In the case under consideration, which is that of large macromolecules, it is more simple to proceed by way of numerical computer calculations of $\delta H_v^E = \delta V_h^E$, δH_h^E and δV_v^E in the integral form of equations (2)–(5) versus the reorientation parameters q and p , for $[l/\lambda] = 1, 0.5, 2$.

As can be seen from Figures 2–11, $\delta H_v^E = \delta V_h^E$ (Figures 2 and 3) is negative for almost all the positive q values; δH_h^E (Figures 4 and 5) is negative for all $q > 0$; whereas δV_v^E (Figures 6–11) is positive at practically all $q > 0$. This is because the orienting field, here, is applied perpendicularly to the plane of observation causing a weakening

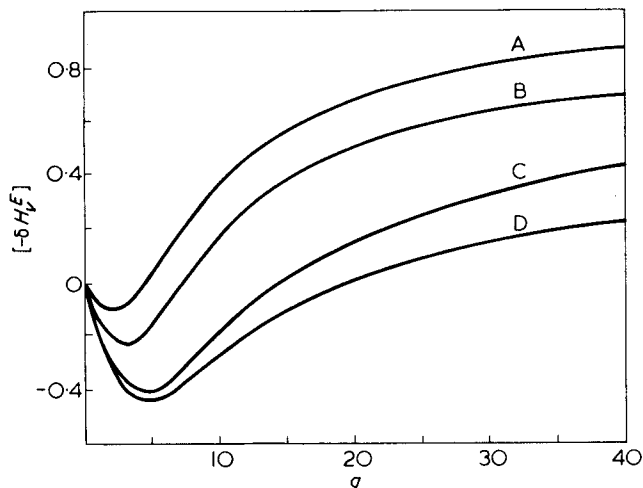


Figure 2 The relative variation $[-\delta H_V^E]$ as a function of the reorientation parameter q , at $p = 0$. A, $l \leq (l/20)\lambda$; B, $l = \lambda/2$; C, $l = \lambda$; D, $l = 2\lambda$

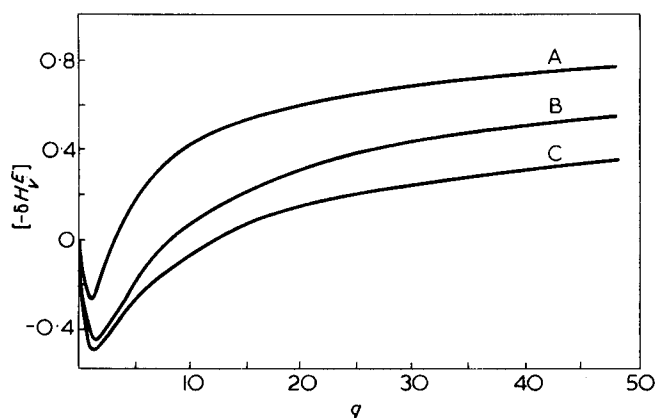


Figure 3 The relative variation $[-\delta H_V^E]$ versus the reorientation parameter q , at $p = 4\sqrt{q}$. A, $l = \lambda/2$; B, $l = \lambda$; C, $l = 2\lambda$

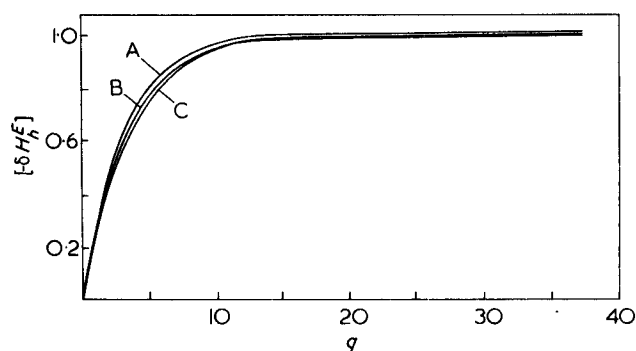


Figure 4 The relative variation $[-\delta H_h^E]$ versus the reorientation parameter q , at $p = 0$. A, $l \leq (l/20)\lambda$; B, $l = \lambda$; C, $l = 2\lambda$

of the horizontal scattered light components and an enhancement of the vertical ones.

The relative variations $\delta V_h^E = \delta H_h^E$ and δV_v^E (Figures 2, 3, 6–11) are strongly dependent on the macromolecular length l . The longer the macromolecule, the larger are the variations, because the scattered light intensity undergoes a weakening due to intramolecular interferences. The weakening is considerably larger if scattered light is observed in the absence of a reorienting field. The depen-

dence on l is less strong in the case of δH_h^E (Figures 4 and 5) since δH_h^E is very small in comparison with δH_h^0 even for macromolecules with $l = 2\lambda$; at very low field strengths, some influence of l on δH_h^E is still apparent, but as E increases δH_h^E very rapidly attains a constant value ($\delta H_h^E \rightarrow -1$), which is now independent of the length of the macromolecule.

With increasing q (i.e. with growing field strength), all relative variations, equations (2)–(5) tend to a finite value when saturation sets in. The saturation phenomenon consists of the complete ordering of the macromolecules in the

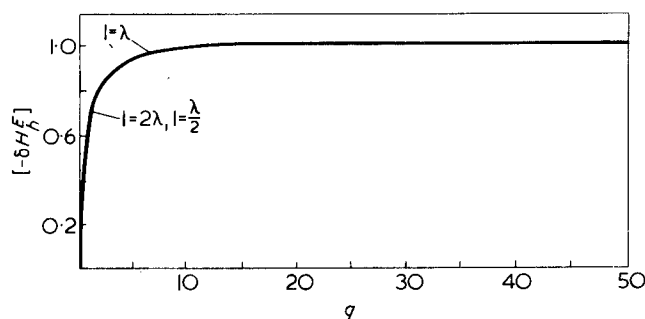


Figure 5 The relative variation $[-\delta H_h^E]$ versus the reorientation parameter q , at $p = 4\sqrt{q}$

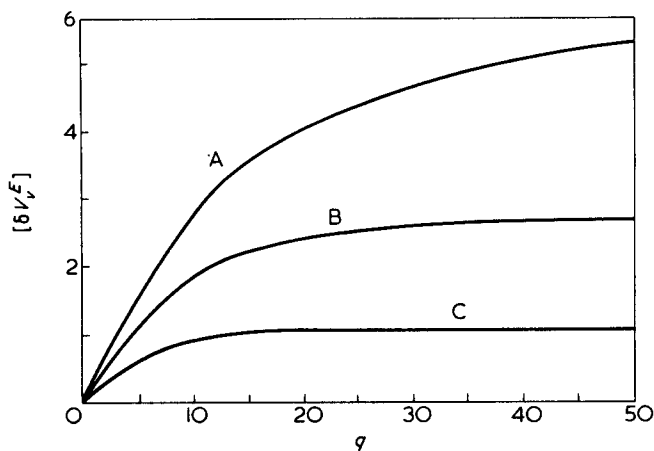


Figure 6 The relative variation $[\delta V_v^E]$ as a function of the reorientation parameter q , at $p = 0$ and $\kappa = 0.1$. A, $l = 2\lambda$; B, $l = \lambda$; C, $l = \lambda/2$

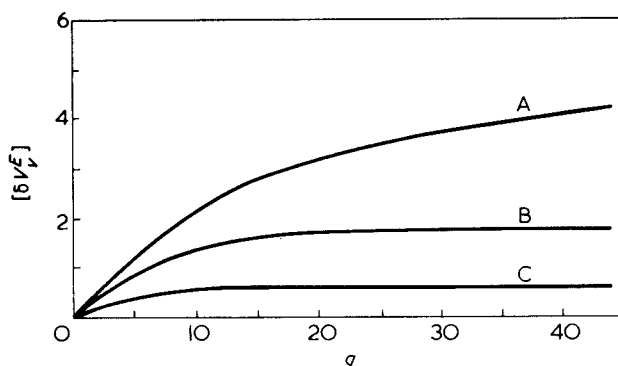


Figure 7 The relative variation $[\delta V_v^E]$ versus the reorientation parameter q , at $p = 0$ and $\kappa = 0$. A, $l = 2\lambda$; B, $l = \lambda$; C, $l = \lambda/2$

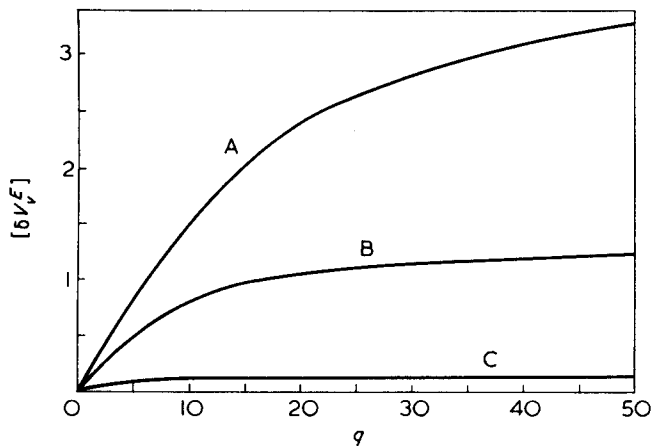


Figure 8 The relative variation $[\delta V_v^E]$ vs. the reorientation parameter q , at $p = 0$ and $\kappa = -0.1$. A, $l = 2\lambda$; B, $l = \lambda$; C, $l = \lambda/2$

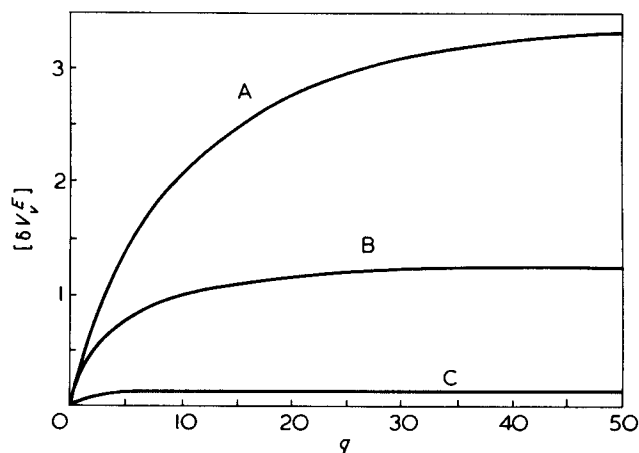


Figure 11 The relative variation $[\delta V_v^E]$ vs. q , at $p = 4\sqrt{q}$ and $\kappa = -0.1$. A, $l = 2\lambda$; B, $l = \lambda$; C, $l = \lambda/2$

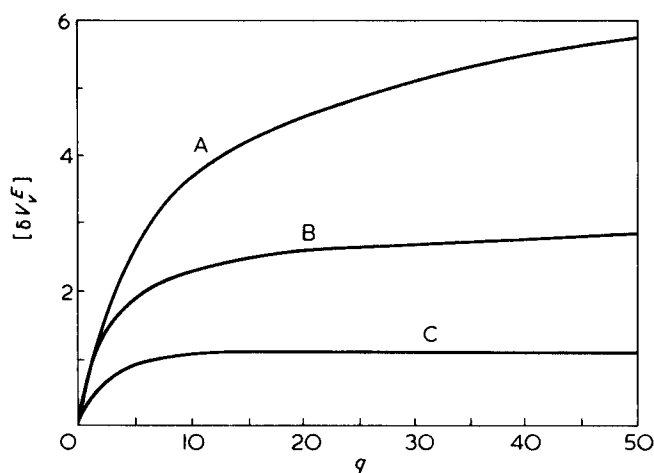


Figure 9 The relative variation $[\delta V_v^E]$ vs. the reorientation parameter q , at $p = 4\sqrt{q}$ and $\kappa = 0.1$. A, $l = 2\lambda$; B, $l = \lambda$; C, $l = \lambda/2$

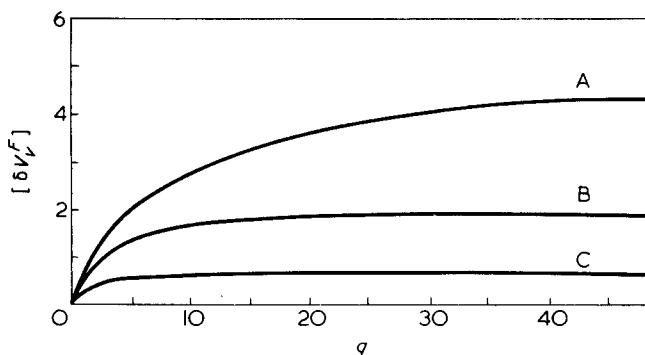


Figure 10 The relative variation $[\delta V_v^E]$ vs. the reorientation parameter q , at $p = 4\sqrt{q}$ and $\kappa = 0$. A, $l = 2\lambda$; B, $l = \lambda$; C, $l = \lambda/2$

external orienting field. At a given temperature T , macromolecules with a given value of electric anisotropy, $(\alpha_3 - \alpha_1)$, attain the completely ordered state more readily the smaller their length l .

In calculating the electric field strength when saturation occurs, the incident wavelength, λ , as well as the electric anisotropy value, $(\alpha_3 - \alpha_1)$, plays a highly essential role. For example, in the case of collagen at a wavelength of the order of 5600 Å the relative variation $\delta H_h^E = \delta V_v^E$ attains the value corresponding to saturation in a field of 30 e.s.u.

whereas δH_h^E attains its saturation value at a field strength of 17 e.s.u.

It is also worth stating that, in absolute values, $|\delta V_v^E| = |\delta H_v^E|$, $|\delta V_v^E|$ and $|\delta H_h^E|$ are always largest for macromolecules possessing a permanent electric dipole moment.

The numerical analysis of the components (equations 2–4) is also applicable to the reorientation of macromolecules by the electric field of laser light, of intensity I_L and frequency ω ¹⁰, when $p = 0$ and $q(\omega) = [(\alpha_3^\omega - \alpha_1^\omega)I_L/2kT]$. Optical molecular reorientation in polymers¹¹ and liquid crystals^{11–14} has, in fact, successfully been observed a short time ago.

Studies of this kind are of considerable importance for the determination of the optical anisotropy of macromolecules, since the relevant formulae involve relative variations, defined by the phenomenon of electric and optical saturation^{9,15}.

In recent years, electric light scattering observations in synthetic and biological polymers^{16,17} as well as liquid crystals¹⁸ have provided abundant, interesting data on the dipole moments of macromolecules and their polarizability anisotropies. Lately, first observations have been reported¹⁹ of the effect of electric fields on the depolarization ratio of light, scattered by molecular liquids.

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