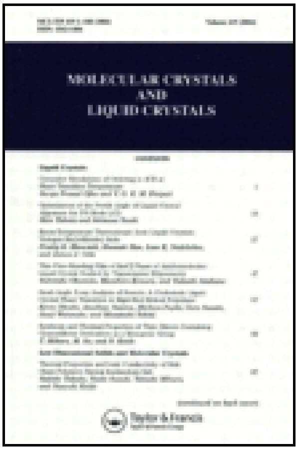

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Determination of the Viscoelastic Constants of Nematic Liquid Crystals by Measuring Line Broadenings of the Scattered Light

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After studying the scattering geometry of nematic liquid crystals, the authors show that an experimental arrangement with optic director in the scattering plane is preferable, and that a considerably strong EE scattered light will be acquired at oblique incidence, which would usually vanish at a 90° incidence. Intensity and linewidth distributions as functions of incident angles are then calculated. Thereby a scheme for determining the viscoelastic constant is proposed, which involves the linewidth measurements of the scattered light only. A MALVERN digital correlator (K7023) is employed for the linewidth measurements. Our optical setting up makes the experimental work easy to do.

Keywords: nematic liquid crystal elastic constants, nematic liquid crystal light scattering

INTRODUCTION

De Gennes[1] pointed out that the director fluctuations of nematic liquid crystals caused the strong depolarized scattered light and that the intensity of the scattered light was given by

$$D_{if} \propto k_B T \sum_{\gamma=1,2} (i_\gamma f_{N0} + I_{N0} f_\gamma)^2 / (K_{33} q_p^2 + K_{\gamma\gamma} q_n^2 + \chi_a \mathrm{H}^2) \quad (1)$$

where

i, **f** are the polarizations of incident light and outgoing light.

K_{11}, K_{22} and K_{33} are the Splay, Twist and Bend Frank elastic constants, respectively.

q_p, q_n represent the components of the scattering vector **q** parallel to and normal to the average director $\mathbf{N}_0$.

$\gamma = 1$ or 2 indicates the two eigen unit directions $\mathbf{e}_1$, $\mathbf{e}_2$.

χ_a is the magnetic anisotropy of NLC, H is the magnetic field applied in the direction of $\mathbf{N}_0$.

As well known, $\mathbf{e}_1$ and $\mathbf{e}_2$ are relevant to the two normal modes of the director fluctuations respectively, and the purely geometric factor $(i_\gamma f_{N_0} + i_{N_0} f_\gamma)^2$ plays an important role in light scattering of NLC, where $i_\gamma = (\mathbf{i} \cdot \mathbf{e}_\gamma)$, $f_{N_0} = (\mathbf{f} \cdot \mathbf{N}_0)$ etc. It is obvious that by measuring the intensity of the scattered light one can determine the Frank constants in principle. Here we report, however, a different approach which is mainly concerned with measuring the line broadenings of the scattered light, and which eventually makes it possible to determine the viscoelastic constants by fitting the linewidths with the following equations.[2,3]

$$1/\tau_1 = (K_{11}q_n^2 + K_{33}q_p^2 + \chi_a \mathrm{H}^2) \times \left[\frac{1}{\gamma_1} + \frac{1}{4}\frac{[1 + \lambda(\cos^2\theta_q - \sin^2\theta_q)]^2}{\nu_3(\cos^2\theta_q - \sin^2\theta_q)^2 + 2(\nu_1 + \nu_2)\sin^2\theta_q\cos^2\theta_q}\right] \qquad (2)$$

$$1/\tau_2 = (K_{22}q_n^2 + K_{33}q_p^2 + \chi_a \mathrm{H}^2) \times \left[\frac{1}{\gamma_1} + \frac{1}{4}\frac{(1 + \lambda)^2}{\nu_2 tg^2\theta_q + \nu_3}\right] \qquad (3)$$

where ν_1, ν_2, ν_3, γ_1, and λ are the viscosity coefficients, θ_q is angle between **q** and $\mathbf{N}_0$, τ_1 and τ_2 are the relaxation time of mode 1 and mode 2.

SCATTERING GEOMETRY

Usually the director of a planar sample cell (or homeotropic) is placed in the scattering plane or vertical to it. An appropriate arrangement should be in such a manner that mode 1 and mode 2 are completely separated so as to facilitate further data processing. Having compared Table 1 and Table 2, we realize that to place the director of NLC in

TABLE I

Geometric factors with director in the scattering plane

Polarizations	$(i_1 f_z + f_1 i_z)^2$	$(i_2 f_z + f_2 i_z)^2$	Information obtained
EE	$(i_1 f_z + f_1 i_z)^2$	$(\mathrm{O} f_z + \mathrm{O} i_z)^2$	1
EO	$(i_1 \mathrm{O} + \mathrm{O} i_z)^2$	$(\mathrm{OO} + f_2 i_z)^2$	2
OE	$(\mathrm{O} f_z + f_1 \mathrm{O})^2$	$(i_2 f_z + \mathrm{OO})^2$	2
OO	$(\mathrm{OO} + \mathrm{OO})^2$	$(i_2 \mathrm{O} + f_2 \mathrm{O})^2$	none

the scattering plane is the correct arrangement. Here we have followed the convention that E refers to polarization of wave in the scattering plane whereas O refers to that vertical to the scattering plane, and EO indicates the experimental configuration where **i** is in the scattering plane, **f** is normal to it, etc. Since we will work on the sample arrangement with optic axis lying in the scattering plane only, O, E can be understood to stand for ordinary, extraordinary waves, and hence n_o, n_e (and ε_o, ε_e) stand for ordinary, extraordinary refractive indices (and dielectric tensor components) which appear in the paper later. If, however, we take a close look at EE configuration of Table 1, we will find that the geometric factor approaches zero in normal incidence, under which observations are often made. Therefore, it seems that information on mode 1 is simply lost. Fortunately, Table 1 does not prevent us from employing oblique incidence where the EE scattered light may be strong enough so as to provide information on mode 1. In fact, a generalization of eq. (1) is[4,5]

$$D_{if} \propto \frac{n_f(\theta_f)}{n_i(\theta_i)\cos^2(\theta_f^r - \theta_f)\cos(\theta_i^r - \theta_i)} \sum_{\gamma=1,2} \frac{G_{if\gamma}}{K_{\gamma\gamma}q_n^2 + K_{33}q_p^2 + \chi_a \mathrm{H}^2)} \tag{4}$$

where all angles of vectors are measured with respect to $\mathbf{N}_0 : S_0$ θ_i is angle of incident wave; θ_i^r is angle of incident ray in the sample, etc.

TABLE II

Geometric factors with director perpendicular to the scattering plane

Polarizations	$(i_1 f_z + f_1 i_z)^2$	$(i_2 f_z + f_2 i_z)^2$	Information obtained
EE	$(i_1 \mathrm{O} + f_1 \mathrm{O})^2$	$(i_2 \mathrm{O} + f_2 \mathrm{O})^2$	none
EO	$(i_1 f_z + \mathrm{OO})^2$	$(i_2 f_z + \mathrm{OO})^2$	1, 2
OE	$(\mathrm{OO} + f_1 i_z)^2$	$(\mathrm{OO} + f_2 i_z)^2$	1, 2
OO	$(\mathrm{O} f_z + \mathrm{O} i_z)^2$	$(\mathrm{O} f_z + \mathrm{O} i_z)^2$	none

When the director is placed in the scattering plane, the geometric factor $G_{if\gamma}$ has three possible values

$$G_{EE1} = \sin^2(\theta_i^r + \theta_f^r);\ G_{EO2} = \sin^2\theta_i^r;\ G_{OE2} = \sin^2\theta_f^r$$

INTENSITY AND LINEWIDTH DISTRIBUTIONS OF SCATTERED LIGHT FROM A PLANAR SAMPLE CELL

To calculate the intensity and linewidth distributions, we first introduce the internal angle of wave vector inside the sample and the external angle before and after going through the sample. A second suffix i or e is used to label them. Assume that NLC behaves like a uniaxial crystal optically with optic axis $\mathbf{N}_0$, we obtain for E light

$$\cos^2\theta_{ii} = \frac{\cos^2\theta_{ie}/n_e^2}{1 - \cos^2\theta_{ie}(1/n_0^2 - 1/n_e^2)}$$

$$\cos^2\theta_{fi} = \frac{\cos^2\theta_{fe}/n_e^2}{1 - \cos^2\theta_{fe}(1/n_0^2 - 1/n_e^2)}$$

for O light

$$\cos^2\theta_{ii} = \cos^2\theta_{ie}/n_0^2$$

$$\cos^2\theta_{fi} = \cos^2\theta_{fe}/n_0^2$$

where n_0, n_e are the ordinary and extraordinary refractive indices. It is not difficult to verify the following results for EE, EO, OE

$$q_p^2 = K_0^2\,(\cos\theta_{ie} - \cos\theta_{fe})^2 \tag{5}$$

and

$$\text{for EE } q_n^2 = K_0^2\,(n_e\sqrt{1 - \cos^2\theta_{ie}/n_0^2} - n_e\sqrt{1 - \cos^2\theta_{fe}/n_0^2})^2 \tag{6}$$

$$\text{for EO } q_n^2 = K_0^2\,(n_e\sqrt{1 - \cos^2\theta_{ie}/n_0^2} - n_0\sqrt{1 - \cos^2\theta_{fe}/n_0^2})^2 \tag{7}$$

$$\text{for OE } q_n^2 = K_0^2\,(n_0\sqrt{1 - \cos^2\theta_{ie}/n_0^2} - n_e\sqrt{1 - \cos^2\theta_{fe}/n_0^2})^2 \tag{8}$$

We have noticed that q_p is independent of polarizations, and does not rely on refractive indices. This can be understood as a consequence of the simple fact, namely, the **K** vector component parallel to the boundary is continuous across the boundary where refraction and reflection take place. Inserting eqs. (5), (6), (7) and (8) into eq. (4) and ignoring the difference between ray direction and wave direction for the time being, we obtain the intensity distributions with θ_{ie}. Fig. 1 gives the distributions of MBBA, where we have assumed $\theta_{fe} = \theta_{ie} + S$, S being the scattering angle which is kept constant. Parameters used are as follows: $n_0 = 1.54$, $n_e = 1.76$; $K_{11} = 6.7 \times 10^{-12}$ Newton, $K_{22} = 4.2 \times 10^{-12}$ Newton, $K_{33} = 8.4 \times 10^{-12}$ Newton; $\nu_1 = 0.508$ poise, $\nu_2 = 0.416$ poise, $\nu_3 = 0.257$ poise, $\gamma_1 = 0.763$ poise, $\lambda = 0.959$. The EE scattered light is very striking: It is symmetrically distributed about $(90° - S/2)$ at which it becomes zero, and the intensity increases as the incident angle moves away

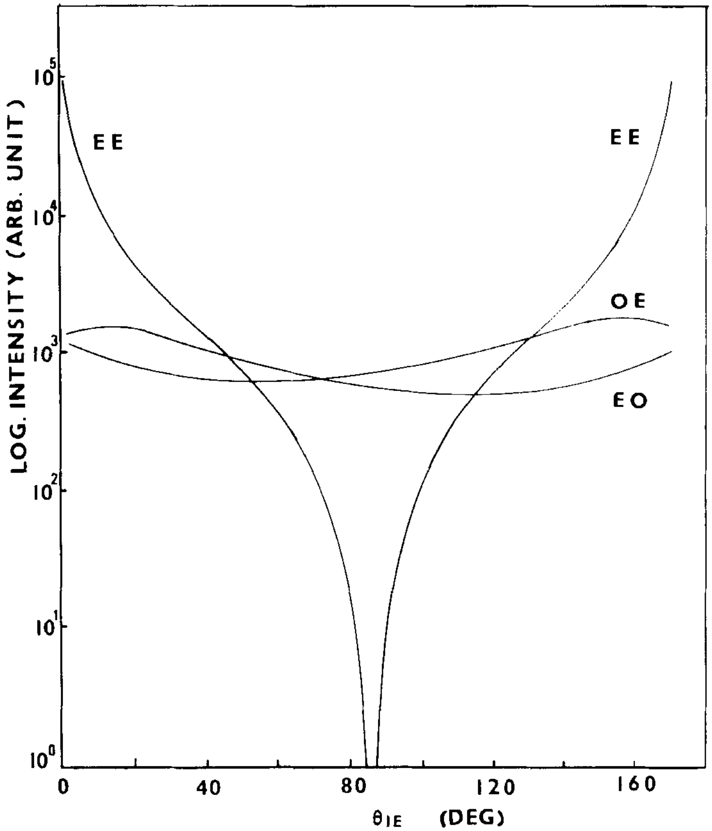

FIGURE 1 Intensity distributions of MBBA at s = 7°. (in arbitrary unit)

from the symmetrical angle. Apparently, the scattered light is not necessarily depolarized, as in the case of EE when at oblique incidence angle other than ($90° - S/2$). On the other hand, the intensity of EO or OE does not vary very much over the whole range of the incident angle.

As well known that the angle α between ray and wave normal in a uniaxial crystal is the same as the angle between electric field **E** and electric displacement **D**, and that $\alpha = 0$ when $\mathbf{E}//\mathbf{N}_0$ or $\mathbf{E} \perp \mathbf{N}_0$. We may expect that α arrives at its maximum somewhere in between. The following calculation shows that $\cos(\alpha_{max})$ is very close to 1 for nematic liquid crystals as long as n_o does not differ from n_e very much. The dielectric tensor ε can be expressed as

$$\varepsilon = \begin{bmatrix} \varepsilon_o & 0 & 0 \\ 0 & \varepsilon & 0 \\ 0 & 0 & \varepsilon_e \end{bmatrix}$$

in an appropriate coordinate system (x, y, z) in which z is in the direction of $\mathbf{N}_0$, x is normal to the scattering plane, then we have

$$\mathbf{D} = \varepsilon \cdot \mathbf{E} = \mathbf{j}\varepsilon_o E_y + \mathbf{k}\varepsilon_e E_z$$

$$cos\ \alpha = \frac{\varepsilon_o E_y^2 + \varepsilon_e E_z^2}{\sqrt{E^2(\varepsilon_o^2 E_y^2 + \varepsilon_e^2 E_z^2)}}$$

assume $E_z^2 = E^2 - E_y^2$, we have

$$\cos\alpha = \frac{\varepsilon_e E^2 + (\varepsilon_o - \varepsilon_e)\, E_y^2}{E\sqrt{\varepsilon_e^2 E^2 + (\varepsilon_o^2 - \varepsilon_e^2)\, E_y^2}}$$

When $(E_y/E)^2 = n_e^2/(n_0^2 + n_e^2)$, $\cos\alpha$ has a minimum $\cos(\alpha_{max}) = 2n_e n_o/(n_0^2 + n_e^2)$; For MBBA, when $\theta_{ii} = 48°49'$, $\cos(\alpha_{max}) = 0.9912$, $\alpha_{max} = 7°38'$. Here we have used the fact $\varepsilon_0 \alpha n_o^2 \approx \varepsilon_e \alpha n_e^2$. Clearly, the calculated small angle ensures the acceptability of our estimate of the intensity of the scattered light with ray direction replaced by wave direction for simplicity.

By inserting q_n^2, q_p^2 into eq. (2) or eq. (3), we obtain the linewidth distributions, see Fig. 2; the main features are: $1/\tau_1$ (EE) is symmetric about ($90° - S/2$), where it arrives at the maximum, and $1/\tau_2$ [EO, $180° - (S + \theta_{ie})$] $= 1/\tau_2(\text{OE}, \theta_{ie})$. On considering the symmetry

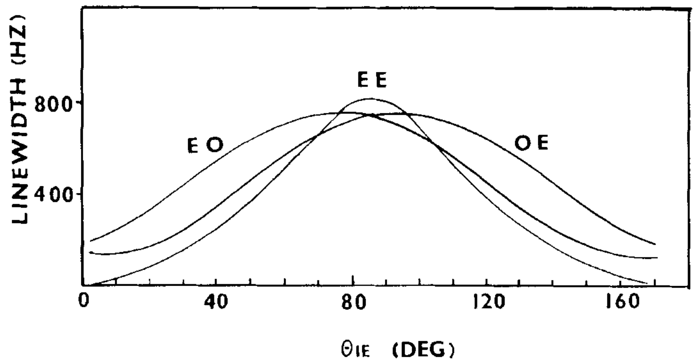

FIGURE 2 Linewidth distributions of MBBA at s = 8°

of the characteristics of the scattered light, it can be understood that $\theta_{fe} = \theta_{ie} + S$ does not lose generality. In fact, an experiment with $\theta_{fe} = \theta_{ie} + S$ is equivalent to that with $\theta'_{fe} = \theta'_{ie} - S$ when $\theta'_{ie} = 180° - \theta_{ie}$, $\theta'_{fe} = 180° - \theta_{fe}$ as N_0 being reversed.

A SCHEME FOR DETERMINING VISCOELASTIC CONSTANTS

By measuring linewidths of the scattered light at various incident angle while keeping the scattering angle fixed, then fitting the measured linewidths with eq. (2) or eq. (3), we may obtain all or part unknowns involved if the incident angle varies at a step small enough and the total number of measurements is large enough. We have tried to fit for K_{11} and K_{33} of MBBA as a demonstration which employed EE scattered light only. Fig. 3 illustrates the experimental setting up. A He-Ne laser beam of 0.95 mw is split by a beam splitter SP, from which a small portion is reflected. The reflected beam, used as a reference beam for the optical setting up, passes through the rotating axis of the table on which the planar sample cell is mounted. The transmitted beam, having reflected by mirror M_1, impinges on the center of the cell at an angle S. F_1, F_2 are two convex lenses of focal length 20 cm. Both beams are focused on the sample cell exactly at the same point on the rotating axis of the table. The illuminated volume is about 0.3 mm in diameter, which is then imaged by the lens F_3 of focal length 10 cm on the pinhole P_1. The scattered light is finally collected by a photomultiplier PMT through the second pinhole P_2 in front of the PMT. The pinholes P_1 and P_2 are 50 μm and 1000 μm in diameter, and set 10 cm apart, so that the area of

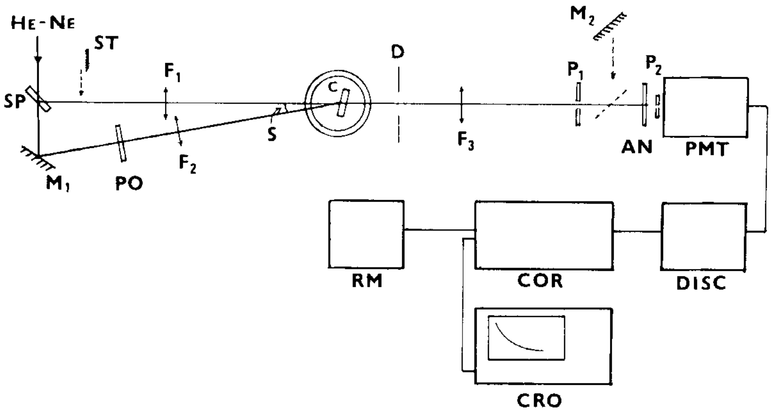

FIGURE 3 The experimental arrangement. SP-beam splitter, ST-stop, D-aperture, F_1, F_2, F_3-convex lenses, M_1, M_2-mirrors, C-sample cell, P_1, P_2-pinholes, PO-polariser, AN-analyser, S-scattering angle, PMT-photomultiplier, DISC-discriminator, COR-digital correlator, RM-ratemeter, CRO-cathode ray oscilloscope.

P_2 is slightly less than one coherence area which is required by correlation technique[6] in order to obtain good correlation. Mirror M_2 is used to check if the scattered light goes right through the pinhole P_1 when moved on to the position indicated by the dotted line. A beam stop ST is used to block the reference beam when observation is in progress. The digital correlator (K7023, Malvern) measures the relaxation time τ_1, τ_2. The measured linewidths of EE scattered light for MBBA are listed in Table 3.

DISCUSSION

The approach described above may suggest a systematical way of determining the viscoelastic constants of NLC by a minimum number of observations on a single sample cell without changing its orientation when a sequence of oblique incidence is employed. We recognize that an attempt to obtain all the constants in one sequence of measurements is extremely difficult: One has to measure linewidths with very small incidence angle step and yet cover a wide range, so that the fine feature of each individual unknown in eq. (2) or (3) is well involved. In addition, one may get in trouble in fitting measured data with eq. (2) or (3), if the measured linewidths vary significantly. There exists, however, flexibility when some of the unknowns are available by other means. In this case, they are replaced by given values in

TABLE III

Linewidths of EE Scattered Light, $S = 7°$, $T = 28 \pm 1.5°C$ MBBA

θ_{ie} (Degree)	$1/\tau_1$ (Hertz)
30	$6.7757 \times 10^{1} \pm 3.0539\ 10^{-1}$
32	$7.1164 \times 10^{1} \pm 3.6224\ 10^{-1}$
34	$8.2759 \times 10^{1} \pm 2.7142\ 10^{-1}$
36	$8.5868 \times 10^{1} \pm 3.6516\ 10^{-1}$
38	$1.0001 \times 10^{2} \pm 6.4429\ 10^{-1}$
40	$1.2502 \times 10^{2} \pm 9.0820\ 10^{-1}$
42	$1.3524 \times 10^{2} \pm 6.2769\ 10^{-1}$
44	$1.4450 \times 10^{2} \pm 9.3360\ 10^{-1}$
46	$1.6365 \times 10^{2} \pm 1.1749\ 10^{0}$
48	$1.6835 \times 10^{2} \pm 1.6352\ 10^{0}$
50	$2.0138 \times 10^{2} \pm 1.1675\ 10^{0}$
52	$2.0052 \times 10^{2} \pm 1.5190\ 10^{0}$
54	$1.8744 \times 10^{2} \pm 2.2636\ 10^{0}$
56	$1.7178 \times 10^{2} \pm 3.3159\ 10^{0}$
58	$2.0969 \times 10^{2} \pm 4.3581\ 10^{0}$

fitting program. As an example, let viscosity coefficients take values on page 6, a computer fitting of data in Table 3 with Eq. (2) gives $K_{11} = 3.95\ 10^{-12}$ Newton, $K_{33} = 4.64\ 10^{-12}$ Newton. Although these results are by no means satisfactory because of failure in making good sample cell and in fixing the scattering angle accurately, the idea involved in the method is of interest. An interesting point is that we have used EE scattered light intentionally to obtain the results. Fig. 4 illustrates comparison of the measured linewidths with the calculated ones. The comparison reveals that the scattering angle is likely to be less than the assumed value $S = 7°$. The method can work on homeotropic sample cells equally well with minor modifications to equations developed in the paper. It is believed that by using a homeotropic sample cell under a proper magnetic field, we would have better data in the measuring linewidths.

Since the scattered light from NLC has a Lorenztian profile, $1/\tau_1$'s in Table 3 were acquired by means of fitting the measured correlation curves with $\exp(-2t/\tau_1)$. The last column gives the standard deviation of $1/\tau_1$. We have noticed that linewidths for $\theta_{ie} \geqslant 50°$ are much scattered, while standard deviations grow larger. This may be explained as follows: As θ_{ie} becomes larger, intensity of EE light decreases rapidly, leaving a poor SNR. Finally, we would like to point out that our optical arrangement makes observations of scattered light very easy. Since the scattering angle is kept fixed, every time when varying the incident angle, we need only to rotate the stage on which the

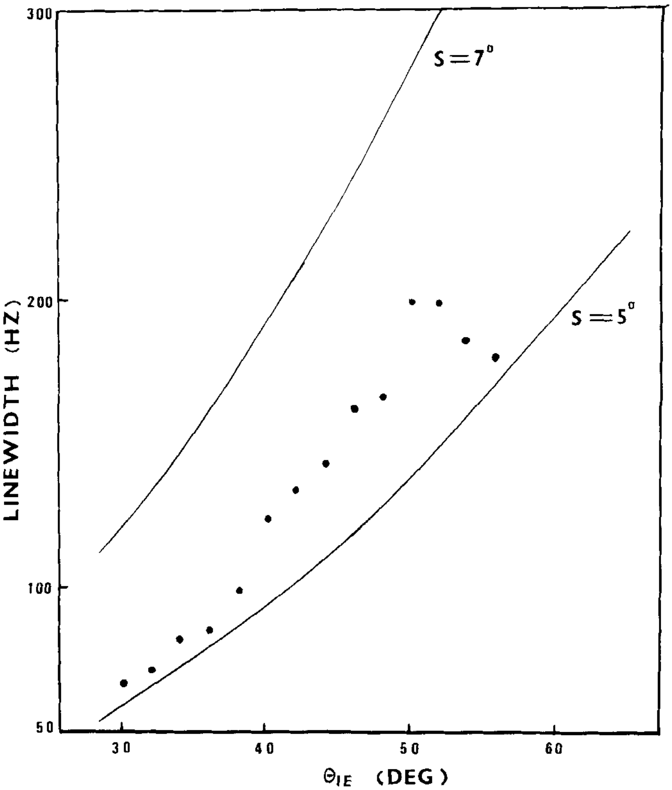

FIGURE 4 Comparison of measured linewidths (dots) at s = 7° and calculated ones (curves) of EE scattered light from MBBA.

sample is held, whereas both the incident and collecting arms remain virtually unchanged.

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