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THE TEMPERATURE DEPENDENCE OF RAYLEIGH-WING SCATTERING FROM LIQUID CRYSTALLINE p-METHOXYBENZYLIDENE-p-n-BUTYLANILINE (MBBA)

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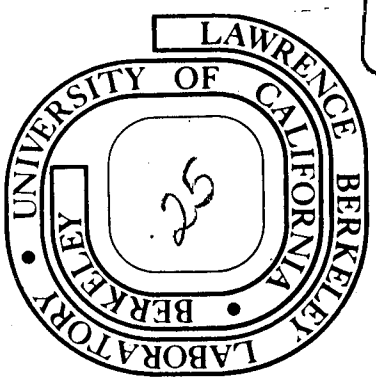

DISCLAIMER

The Temperature Dependence of Rayleigh-Wing Scattering From Liquid Crystalline p-Methoxybenzylidene-p-n-Butylaniline (MBBA)

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ABSTRACT

We have investigated the temperature dependence of Rayleigh-wing scattering in nematic MBBA. Our results are interpreted in terms of the orientational fluctuations of individual molecules, modified by coupling to neighboring molecules.

Nous avous étudié la dépendence en temperature de la diffusion de l'aile Rayleigh dans la phase nématique de MBBA. Nous interpretons nos resultats en termes de fluctuations de l'orientation de molecules individuelles, modifiées par le couplage avec les molecules voisines.

Light scattering as a probe of the various dynamic properties of liquid crystals has been proven to be a powerful technique.[1-6] While most published work deals mainly with scattering from low-frequency thermal fluctuations, little attention has been given to the investigation of high-frequency fluctuations. This is particularly true for Rayleigh-wing scattering. Such an effect arises basically from orientational fluctuations of the individual anisotropic molecules.[7]

In this paper, we report on what we believe to be the first investigation of Rayleigh-wing scattering in liquid-crystalline materials.[8] We are particularly interested in the change of the Rayleigh-wing spectrum as the temperature varies near the isotropic-nematic phase transition. We found that the spectrum can be decomposed into two Lorentzians, one having a halfwidth of a few cm^{-1}, and the other one order of magnitude broader. Both Lorentzians narrowed appreciably as the temperature was lowered, but there was a sudden increase in the linewidths at the isotropic-to-nematic transition. The results are interpreted in terms of the fluctuations of the orientation of individual molecules as modified by the coupling to neighboring molecules.

The experimental arrangement was typical of a Raman scattering setup which has been described previously.[9] An iodine filter cell was used to reduce elastic scattering and a spectral resolution of ~ 1.5 cm^{-1} was chosen for the experiments. The nematic material investigated was para-methoxybenzylidene-para-n-butylaniline (MBBA) and was purified by vacuum distillation. To minimize decomposition, the scattering cell was kept under dry nitrogen atmosphere. The nematic-isotropic transition temperature was frequently checked and was found to remain unchanged.

Through thermal control, the sample temperature was always stabilized to within ± 0.025°K.

An example of the Rayleigh-wing spectra of MBBA is shown in Fig. 1. In analyzing the results, we first deconvoluted an experimental spectrum with the slit function of the monochromator to obtain the true spectrum of the scattered light. We then found that the spectrum could be best fit by a superposition of two Lorentzian lines, as in the case for most ordinary liquids.[7] From the least square fit, we have deduced the linewidths of the two Lorentzians as a function of temperature as shown in Fig. 2. Both Lorentzians become narrower as the temperature approaches the isotropic-nematic transition from the isotropic liquid side. At the transition, there is an abrupt increase in the widths followed by a decreasing trend as the temperature is lowered further, but there is no evidence of critical divergent behavior.

We have plotted the integrated intensities of both Lorentzians as a function of temperature in Fig. 3. The intensity of the narrow component remains constant with decreasing temperature while that of the broad component increases slightly. Compared with the extremely narrow central component studied by Stinson and Litster,[6] these two components have integrated intensities four orders of magnitude weaker. The broad component is 0.87 times as intense as the narrow component at 52°C. At the phase transition, there appears to be a sudden increase in the scattering intensity. Because of the scattering loss at the phase transition, it was difficult to measure the intensity changes quantitatively. In the nematic phase, a Raman mode at 38 cm^{-1} also complicates the intensity measurements of the broad Lorentzian component.

We found the depolarized ratio of the scattered light to be 3/4 for the isotropic and nematic phases. It was independent of the frequency of the scattered radiation. This depolarization ratio is characteristic of light scattered from anisotropic fluctuations.[7]

Recently, Flytzanis and Shen[10] have shown that orientational fluctuations of anisotropic molecules in liquid crystalline materials can give rise to both the very narrow central component studied by Stinson and Litster[6] and the broad Rayleigh-wing component in the scattering spectrum. The very narrow central component arises from orientational fluctuations of molecules under the influence of the mean field created by intermolecular interaction (also known as order-parameter fluctuations). It shows the critical behavior at the liquid-nematic transition. The Rayleigh-wing component arises from orientational fluctuations of individual molecules modified by coupling with neighboring molecules, and have no critical behavior. The theory suggests that the narrow central component is 10^4 times stronger than the Rayleigh-wing component in agreement with our experimental results. The spectrum of the Rayleigh-wing component is given by[10]

$$I(\Omega) = \frac{T}{T^2 + T_c^2}\left[\frac{A\tau_A}{1 + \Omega^2\tau_A^2} + \frac{B\tau_B}{1 + \Omega^2\tau_B^2} + \ldots\right] \qquad (1)$$

where T is the temperature, T_c is the liquid-nematic transition temperature, $\tau_A = \alpha_A\eta(T)/kT$, $\tau_B = \alpha_B\eta(T)/kT$, $\eta(T)$ is the shear viscosity, and A, B, α_A, and α_B are constant coefficients independent of temperature.

Suppose that the first two terms in Eq. (1) describe the two broad Lorentzian components we have observed. In Fig. 2, we have plotted the theoretical curves for the halfwidths $1/\tau_A$ and $1/\tau_B$ as a function of temperature using $\eta(T)$ determined by Martinoty et al.[11] and α_A and α_B as adjustable parameters. The agreement between theory and experiment is fairly good. The sudden increase of the halfwidths at the phase transition is due to the sudden decrease of $\eta(T)$.

Equation (1) also suggests that the integrated intensities of the two components are nearly independent of temperature. As shown in Fig. 3, this is true for the narrower component, but is not so true for the broader component. We should however notice that the theory was developed by using simplifying assumptions on intermolecular interaction. A calculation with more realistic intermolecular interaction may lead to somewhat different results, especially for the broader component. It is also possible that the observed spectrum is actually a superposition of many Lorentzian components such that more terms in Eq. (1) must be taken into account. The additional terms may have stronger temperature dependence.

Our experimental results can also be explored by the usual theory of Rayleigh-wing scattering involving rotational diffusion and libration of molecules.[7,12] However, as is well-known, such a theory is lack of internal consistency and requires more parameter fitting. Therefore, we shall not discuss here how it fits with the experimental data.

In conclusion, we have shown experimentally that the Rayleigh-wing scattering due to basically orientational fluctuations of individual molecules also exists in liquid crystalline materials, in addition to

the strong scattering due to fluctuations of the orientational order parameter.

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FIGURE CAPTIONS

Fig. 1. Typical Rayleigh-wing spectrum of MBBA (T = 51.35°C, slit with = 1.5 cm^{-1}).

Fig. 2. Linewidths of the two Lorentzians as a function of temperature. Circles are experimental data points.

Fig. 3. Inverse of the integrated intensities of the two Lorenztians as a function of temperature. Circles are experimental data points.

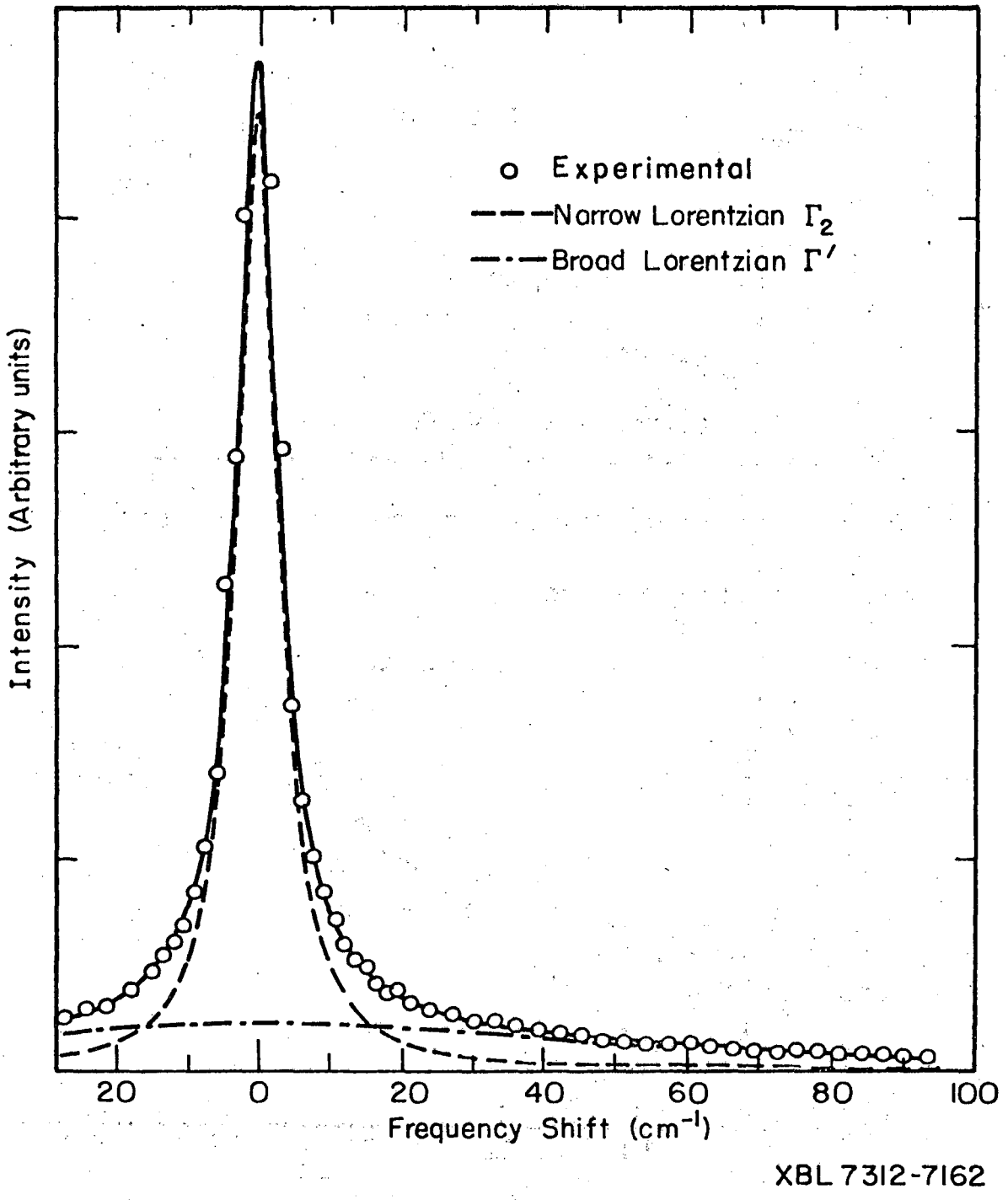
o Experimental
---Narrow Lorentzian Γ_2
—·—Broad Lorentzian Γ'
Intensity (Arbitrary units)
20
0
20
40
60
80
100
Frequency Shift (cm^{-1})
XBL 7312-7162

Fig. 1

Fig. (1)

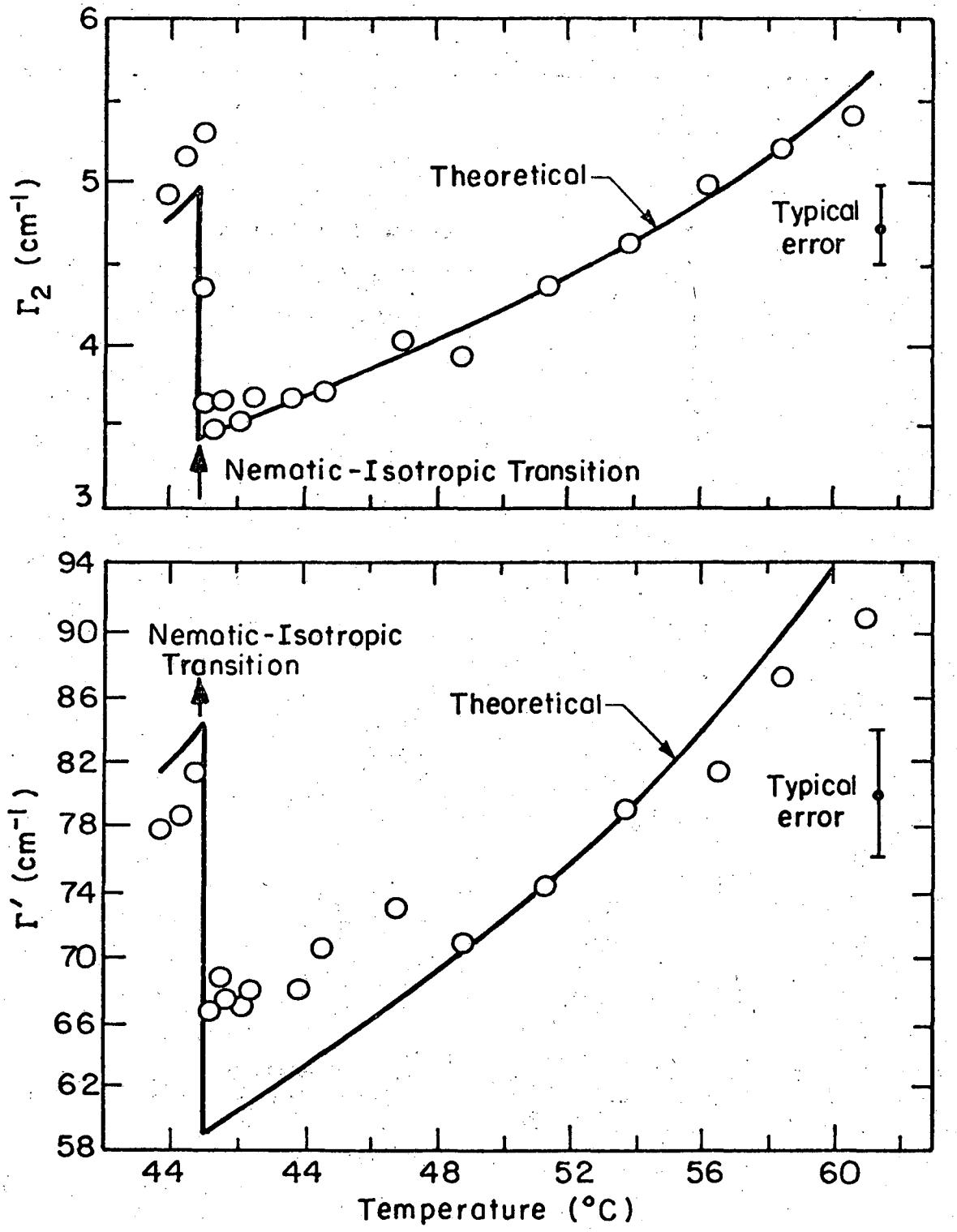

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Fig. 2

Fig.(2)

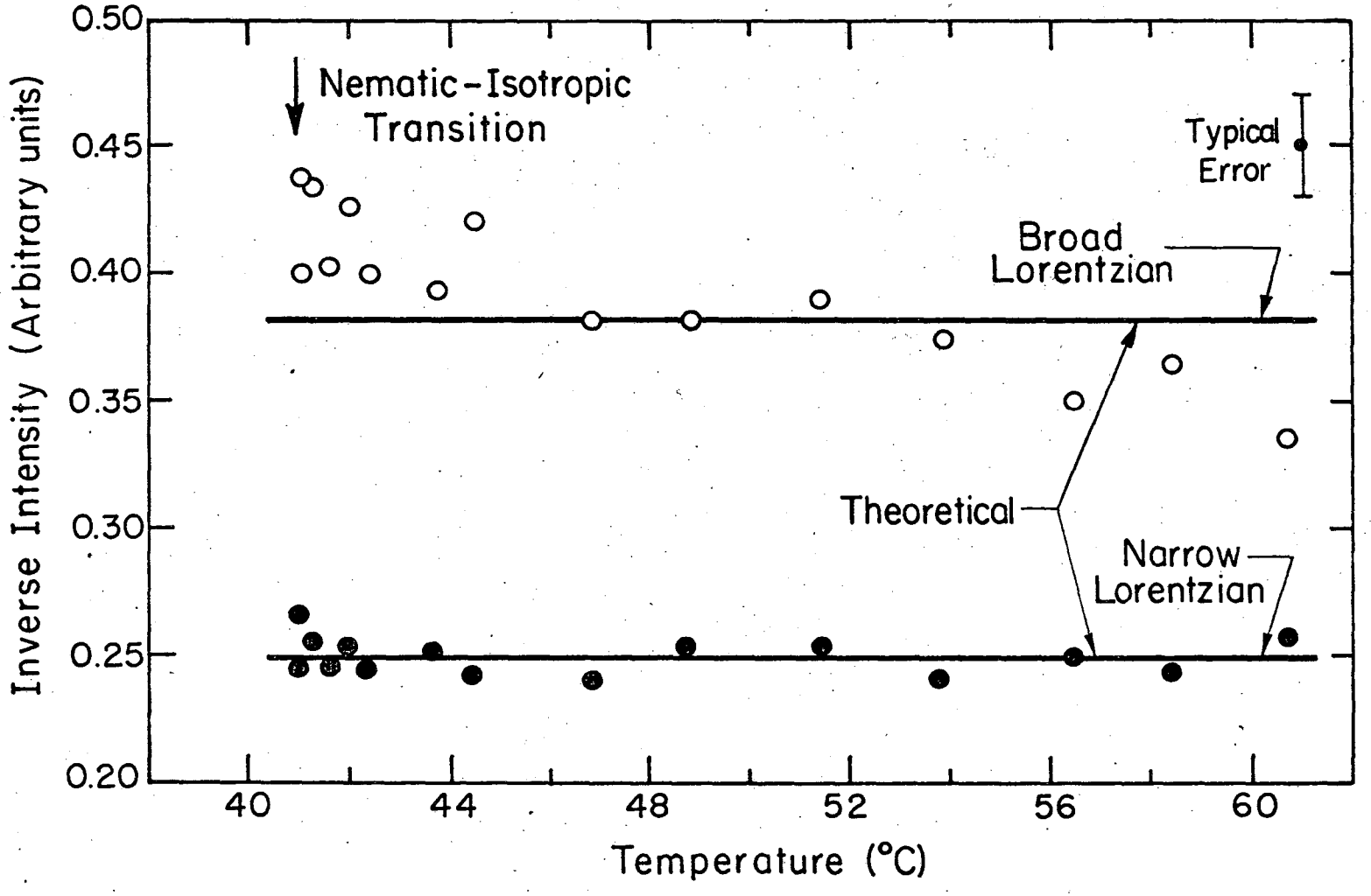

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Fig. 3

Fig. (3)

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