

Light Beating Spectroscopy of Polarized and Depolarized Scattering in *p-n*-hexyl *p'*-cyanobiphenyl

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(Received 8 March 1993)

Both polarized and depolarized light scatterings were observed in the isotropic phase of *p-n*-hexyl *p'*-cyanobiphenyl (6CB) with a new technique of optical beating spectroscopy, in which a Fabry-Pérot etalon was replaced with a spectrum analyzer. This technique is very useful for Rayleigh and Brillouin scattering over the range, at present, from 10^4 to 10^9 Hz with a resolution as high as 1 kHz if needed. The result in 6CB was correlated with the equation derived from the theories by de Gennes and also by Alms *et al.* The observed spectra were in a remarkable agreement with the theoretical prediction, giving strong support to the theories.

PACS numbers: 33.80.-b, 33.20.Fb, 83.70.Jr

The light scattering system with a scanning Fabry-Pérot interferometer and a high-sensitivity photomultiplier has long been the general standard of all the Brillouin scattering experiments ever since Fleury and Chiao first succeeded in the observation of a Brillouin triplet in the middle of the 1960's [1]. Every endeavor has been made to improve the resolution of the experiment, which has not generally been considered satisfactory. A very sophisticated system in which a computer controls multipass Fabry-Pérot etalon or etalons in tandem, for example, has been developed. To reduce the additional line broadening introduced by the spectral width of the light source, a single longitudinal mode laser with a frequency-stabilizing device has been utilized, the resultant lack of output power being compensated by the increased detection sensitivity of a cooled photomultiplier tube followed by a photon counter. The Brillouin scattering system of today is thus becoming more and more complicated though its essential part still stays within the experiment of Fleury and Chiao. Nevertheless, all these efforts to achieve higher resolution seem to have been rewarded with rather limited success.

On the other hand, the idea of a Brillouin scattering experiment based on a completely different principle has been proposed, i.e., the technique of light beating spectroscopy in which the Fabry-Pérot etalon is replaced with a spectrum analyzer. Various experiments have been tried along this line, but most of them were unsuccessful with only one exception. To our knowledge, Eden and Swinny were the first to report success [2]. They skillfully used the stray scattered light as a reference light of the optical heterodyne and obtained clear Brillouin peaks around 30 MHz in Xe near its critical point. This study was a great epoch in the history of Brillouin scattering though not succeeded by followers.

Last year we developed a new type of light beating technique for dynamic light scattering measurements [3,4]. We have already made some experiments with a prototype of this system and checked its fundamental operation by observing Brillouin spectra in water, toluene, and carbon disulfide. The result, which showed a very

high resolution far over the limit of the optical interferometer, was quite satisfactory. The uncertainty in the frequency axis of the scanning etalon was removed by the accurate and reliable sweep of the spectrum analyzer. Now we have finished the system for hyper-resolution spectroscopy over the frequency range, at present, from 10^4 to 10^9 Hz [4]. In this Letter, we report the result obtained in liquid *p-n*-hexyl *p'*-cyanobiphenyl (6CB). The choice of this liquid as a specimen has a twofold meaning. A very fine and complicated structure was expected in the spectrum shape of the light scattering in this liquid for a reason given later. We would be able to test and demonstrate the resolution and overall performance of this system through the experiment in this liquid. The second reason, and perhaps more important than the first, is for the purpose of examining those theories by de Gennes [5,6] and by Alms *et al.* [7] which give a theoretical prediction to the spectrum of the depolarized light scattering. We made an elaborate experiment for these two purposes.

We briefly describe the experimental system. The output of an Ar⁺ laser is split into two beams, which meet again within the specimen; one as an incident light and the other as a reference light of the heterodyne detection. A high-speed photodiode (Hamamatsu S2381) is placed so that its active surface is illuminated by the reference beam. The scattering occurs in the crossing volume, and only the component which goes along with the reference beam generates beat current at the photodiode. The beat signal is received with a spectrum analyzer (Advantest TR4135), and its internal frequency (IF) output is square-law detected and set to a lock-in amplifier, which picks up the very weak beat signal hidden under the shot noise which occupies more than 99% of the IF signal.

This cross-beam geometry would be the most stable configuration of an optical heterodyne that one could think of: The scattered light is superposed with the reference light *at the point* and takes exactly the same optical path thereafter; any disturbance on the path has the least influence on the signal. Further, the scattering angle θ is sharply defined and can be measured as the crossing an-

gle of the two beams. The resolution is determined with the bandwidth of the spectrum analyzer, which can be made narrower than 1 kHz. A half wave plate put on the path of the reference beam rotates its polarization plane by 90° to detect the depolarized VH scattering. Thus nondepolarized VV scattering and VH scattering can be observed alternatively. There is another point in this cross-beam geometry. One can put an acousto-optic (AO) modulator into the reference beam and readily shift its frequency by 160 MHz. This modulation is necessary in the observation of spectra distributing on both sides of the central frequency. If otherwise, and the reference light has the same frequency as the incidence, two spectral components on both sides equally apart from the center would contribute to the beat signal at the same frequency: One cannot discriminate between them. In the present system, Stokes and anti-Stokes components, for example, can be observed separately at different beat frequency.

This specimen, 6CB is a "nematogen" which undergoes a phase transition to a nematic liquid crystal. The measurements were made in its isotropic phase at temperatures above the transition point at 29.3°C . Molecules of this liquid are characterized by a strong interaction between the neighbors with respect to molecular rotation. The rotational motion is likely to involve many others and take place in a cooperative manner with a large effective inertia. A local orientation brought about by fluctuation in a microscopic region would diffuse with a rather long correlation time. In addition is the fact that this molecule is highly polarized and anisotropic from a dielectric point of view. Consequently, the fluctuation in molecular orientation causes the fluctuation in the dielectric tensor: The diffusion process of the fluctuation could be observed through the light scattering, both polarized and depolarized.

Figure 1 shows an example of the spectra observed in 6CB at 48.5°C . The scattering angle is $\theta = 1^\circ 00'$. Figures 1(a) and 1(b) show the whole spectrum of polarized VV and depolarized VH scattering, respectively. Both spectra are marked by a strong central component with the same width, 10.0 MHz. The instrumental width of this observation is only 30 kHz and these curves yield the true spectral width accurately to 0.3%. The diffusion process of the local molecular orientation gives rise to those central peaks in VV and VH spectra through the fluctuation in a diagonal and an off-diagonal component of the anisotropic dielectric tensor, respectively. It is natural that they have the same width, reflecting the decay of the same origin. This kind of VV and VH scattering due to molecular reorientation happens also in many other liquids, but the diffusion in normal liquids is so quick that it gives very broad Rayleigh winds which are usually superposed many times by Fabry-Pérot orders and observed as a raised background level of the spectrum.

Two small phonon peaks are seen in the VV spectrum

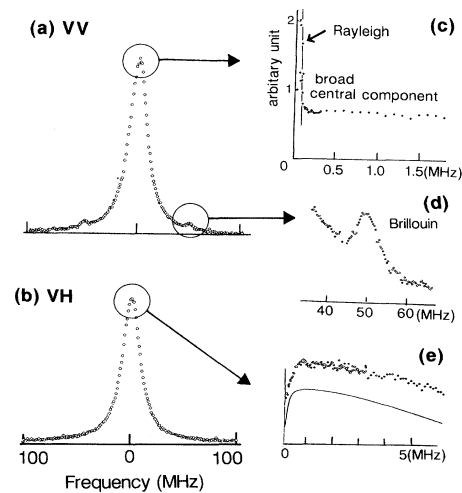


FIG. 1. Example of spectra obtained in 6CB at 48.5°C . The scattering angle is at $\theta = 1^\circ 00'$. (a), (b) The whole shape of the polarized VV and the depolarized VH spectra, respectively, observed with a resolution of 30 kHz and a sampling at every 1 MHz. (c)–(e) Detail of the parts indicated by the circles in (a) and (b) in an increased resolution and sampling: (c) shows a part of the Rayleigh component, (d), the anti-Stokes Brillouin component, and (e), the sharp dip at the center of the VH spectra together with the theoretical curves calculated by Eq. (1) with the parameters given in the text.

superposed with the foot of the central peak. Figure 1(d) is a detailed view of the anti-Stokes component. The peak frequency and its dependence on θ are in agreement with the ultrasonic velocity in this liquid after the shrinkage effect by the inclined base line is corrected. A very careful inspection of the VV curve reveals a sudden rise towards the center in its close vicinity as shown in Fig. 1(c). This sharp spike on the top of the central peak is the one commonly referred to as the Rayleigh component. It is difficult, however, to estimate the half-width of the Rayleigh peak in the absence of its true peak value, which would be overwhelmingly higher than phonon peaks. This very strong contrast in the height of the Rayleigh peak over Brillouin peaks is common to most liquids but water.

The most remarkable feature is hidden at the center of the VH curve. There is a sharp negative spike as shown in Fig. 1(e) that can be found only with an increased resolution as high as 1 kHz and a close sampling at every 30 kHz. This dip has a width ~ 240 kHz at this scattering angle. de Gennes [5,6] and Alms *et al.* [7] independently treated the dynamics of liquids in which local reorientation is coupled with shear viscous flow. The two theories consistently lead to the following equation predicting the power spectrum of the VH scattering, which is to be compared directly with the present experiment:

$$I_{VH}(q, \omega) \propto \frac{\Gamma}{\omega^2 + \Gamma^2} \sin^2 \frac{\theta}{2} + \frac{\Gamma[\omega^2 + (\eta q^2/\rho)^2(1-R)]}{[\omega^2 - \Gamma(\eta q^2/\rho)]^2 + \omega^2[\Gamma + (\eta q^2/\rho)(1-R)]^2} \cos^2 \frac{\theta}{2}, \quad (1)$$

where $q = 2k \sin(\theta/2)$, k being the optical wave number, ω the angular frequency, Γ the width associated with the decay rate of the local orientation, η the viscosity, ρ the density, and R a phenomenological parameter introduced as a measure of the coupling between the reorientational motion and the viscous flow. The first term of this equation is safely ignored in the present experiment in which θ is less than 10° . When $\eta q^2/\rho \ll \Gamma$ holds, as is the case in Fig. 1, the second term can be roughly sketched as a broad Lorentzian curve with a dip at its center. The Lorentzian broadening gives Γ and the width of the dip, $\eta q^2/\rho$, the decay rate of the viscous flow. The solid line in Fig. 1(e) represents the theoretical curve calculated with those parameters Γ , η/ρ , and R determined and given later. The curve successfully describes the observed spectrum.

The VH spectra observed at different scattering angles are shown in Fig. 2(a). The dip whose width is proportional to q^2 rapidly broadens as θ increases, while the total width keeps almost constant. The solid lines are the theoretical prediction of Eq. (1) calculated with $\Gamma/2\pi = 10.0$ MHz determined from the respective VV curve, $\eta/\rho = 1.7 \times 10^{-3}$ m²/s, and $R = 0.30$ determined in the fitting to the spectrum. It should be emphasized here that the same values of Γ , η/ρ , and R were used in all four theoretical curves in Figs. 1(e) and 2(a). The equation including only one adjustable parameter R marvelously reproduces the spectra. Figure 2(b) shows a series of VH spectra for $\theta = 1^\circ, 2^\circ, 3^\circ, 4^\circ$ observed at 35.1°C , by 5.8°C above the transition to the ordered phase of nematic liquid crystal. The molecular reorientation motion would slow down and $\Gamma/2\pi$, hence the total width decreases to 1.90 MHz. The dip width, on the oth-

er hand, is proportional to η and increases as temperature decreases. The spectrum gradually changes its shape as θ increases and loses the characteristic form with a central dip as shown in the lowest curve in Fig. 2(b). The solid lines are the theoretical curves of Eq. (1) calculated with $\eta/\rho = 3.0 \times 10^{-3}$ m²/s, $\Gamma/2\pi = 1.9$ MHz, and $R = 0.23$. Alms *et al.* have already reported a series of intensive works of depolarized light scattering in liquids [7] and solutions [8]. In particular, they observed anisaldehyde in the GHz region and obtained spectra with a shape quite similar to Figs. 1 and 2. Their spectra showed very good agreement with the theoretical curve of Eq. (1) after it was convoluted with the instrumental spectrum of the Fabry-Pérot. The present experiment with hyper resolution provided us with a direct comparison with theory, giving further support to it.

These somewhat strange spectra can be physically understood if considered in the time domain. Once a local orientation arises spontaneously by fluctuation, it gives an off-diagonal component $\Delta\epsilon_{ij}$ in the dielectric tensor which would cause the VH rotation of the polarization. This anisotropy $\Delta\epsilon_{ij}$ then decays in a quick process of reorientation. This local rotation of reorientation causes a viscous flow which, in turn affects $\Delta\epsilon_{ij}$ through a microscopic flow birefringence effect, and accelerates the decay of $\Delta\epsilon_{ij}$. This flow itself decays very slowly with a viscous loss (under the condition $\eta q^2/\rho \ll \Gamma$). The situation is schematically illustrated in Fig. 3: The decay of $\Delta\epsilon_{ij}$ overshoots itself, dragged by the viscous flow. The Fourier transform of this curve makes a superposition of two Lorentzian curves upward and downward with width

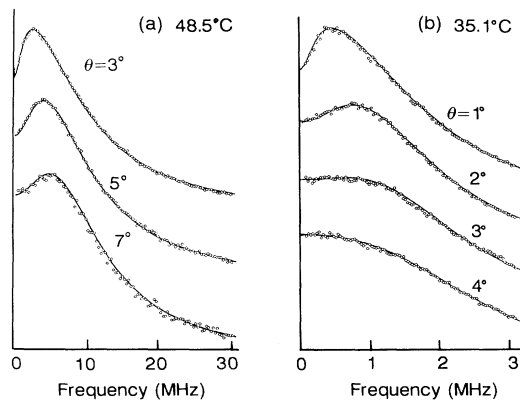


FIG. 2. Depolarized VH spectra observed at various scattering angles (a) at 48.5°C and (b) at 35.1°C . The solid lines show the theoretical prediction of these spectra calculated by Eq. (1) with the required parameters given in the text.

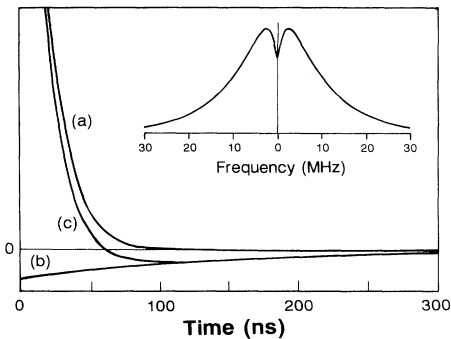


FIG. 3. Schematic illustration showing the decay of correlation function of $\Delta\epsilon_{ij}$, the fluctuation in an anisotropic dielectric constant, and the corresponding power spectrum (inset). Curve a is associated with the decay of local orientation, b , the decay of the coupled viscous flow, and c shows the overshooting decay of $\Delta\epsilon_{ij}$. All these curves are numerically calculated to be directly compared with the spectrum at 48.5°C and $\theta = 3^\circ$ shown in Fig. 2(a).

Γ and $\eta q^2/\rho$, respectively, as shown in the inset. This is a phenomenological story, however, that can be told without any knowledge of the nature of the molecule of interest. In the next stage, R and Γ should be considered on the basis of the statics and dynamics of molecules: What is actually happening at the molecular level?

Finally a remark should be given on the high resolution of the light beating technique shown in this study. Generally speaking, light scattering studies are to make the most of light whose frequency is as high as 10^{14} Hz. This high-energy carrier wave goes into the field of fluctuations, and carries back the information of interest. The Fabry-Pérot interferometer, as an optical filter, treats the signal whose frequency is that high. If an accuracy of 1 MHz is needed, a relative resolution of $\sim 10^{-8}$ is strictly required. In the light beating technique, on the other hand, the carrier is removed by the optical mixing process, and only the bare signal typically at $\sim 10^9$ Hz is taken up and sent to the electronic apparatus for the frequency analysis. Then the relative resolution required for 1 MHz accuracy is reduced to 10^{-3} , the easiest requirement for a spectrum analyzer. Whether to treat a signal with the carrier or without is the intrinsic difference which gives high contrast to the resolution.

The comparison of the resolution between them would not be simple or straightforward, however. The quality of the spectra by the Fabry-Pérot technique is determined mostly by finesse and scanning linearity. In the light beating technique, the bandwidth of the receiver is the factor to be compared with them. Suppose here that a phonon peak at 1 GHz is observed with a Fabry-Pérot etalon with finesse 100, for instance. The optimum free spectral range is around 3 GHz and hence the expected resolution is 320 MHz. It would not make sense, however, to compare this value with the bandwidth of the spectrum analyzer which can be narrower than 1 kHz. The fact is that the overall resolution is effectively determined not by the bandwidth, but by the angular divergence of the light source with a finite beam diameter. This problem is unavoidable and common to all the light scattering experiments: The uncertainty in the scattering angle introduces an additional spectral width through, for example, the dispersion relation between q and ω . After all, it could be said in the comparison of the resolution that the new technique can have a power more than two decades higher than the previous ones.

Unfortunately the spectral range is limited below 1

GHz at present: The highest phonon is observed at 1.007 GHz so far in carbondisulfide [4]. This limiting frequency is actually determined by the photodiode, which must have the characteristics of both high speed and high sensitivity. These two demands are often contradictory. Development of a new photodiode useful in the full GHz region would give one solution to this problem, but what is more practical is to make use of the reference light whose frequency can be readily changed. If the modulation frequency could be increased to the GHz range, the beat frequency for GHz phenomena would be reduced down into the pass band of the present photodiode. We have a plan to use a SAW (surface acoustic wave) device as a GHz modulator for this purpose. Further, the pursuit of this idea would lead to a complete optical superheterodyne system of literal sense, in which the receiver is sharply tuned at a certain IF frequency while the reference light sweeps its frequency as a local oscillator. It would be realized in the near future with the development of such a device as to sweep the laser frequency freely over the GHz range, when the Fabry-Pérot etalon would finish its duty as a spectrometer of the light scattering experiments.

This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

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