LINE BROADENING OF LIGHT SCATTERED FROM A LIQUID SURFACE*

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We report results of a spectral analysis of light scattered by a liquid surface. These results are consistent with the assumption that thermally excited surface waves are responsible for the scattering, and the phenomenon may be regarded as the surface-wave analog of ordinary Brillouin scattering in the bulk of a fluid. Scattering of light from thermal surface waves on a liquid surface, without regard to spectral distribution, was first predicted by Smoluchowski.[1] It was observed experimentally by Mandelshtam,[2] and later by Raman and Ramdas,[3] and discussed further by Gans,[4] and by Andronow and Leontowicz.[5]

The classical dispersion relation for surface phonons, in contrast to phonons in the bulk of the liquid, does not involve bulk viscosity (compressional relaxation effects), and the decay of the surface waves is determined primarily by shear viscosity. At the small surface wavelengths of interest ($\lambda \simeq 10^{-5}$ cm) the role of viscosity in the dispersion relation is no longer so small that it can be described as a first-order correction, as is ordinarily done, but the complete form of this relation must be used. As is known,[6] the temporal decay of a surface wave of the form $\exp(iKx)\exp(St/\tau_0)$ is obtained from the relation

$$S^2+2S-(1+2S)^{1/2}+1+y=0,$$

where $y=(\omega_0\tau_0)^2$, $\omega_0{}^2=\sigma K^3/\rho$, $\tau_0=\rho/2\mu K^2$, $K=2\pi/\Lambda$, ρ = mass density, σ = surface tension, μ = shear viscosity, and Λ = wavelength. This equation has been solved numerically and the real and imaginary parts of the two roots appropriate to our problem are shown as a function of y in Fig. 1. For $y>0.145$ the decay is oscillatory (the two roots are complex conjugates), but for $y\leqslant 0.145$ we have $\operatorname{Im}S=0$, so that the waves are overdamped, and the two modes decay at different rates. When light is scattered from thermally excited surface waves, we expect a Brillouin doublet to result from the underdamped waves but only a spectral broadening from the overdamped waves.

The scattered intensity from a liquid surface is ordinarily quite weak and difficult to analyze with standard means unless the incident and scattered beam directions are chosen properly. Calculation of the intensity of the scattered light indicates that the intensity is greatest at "forward" scattering angles in the neighborhood of the specular direction. This is related, in part, to the fact that the mean-square surface displacement is proportional to Λ^2. Also, we find that in transparent liquids the scattering is enhanced if the light beam is totally reflected from the surface and observation is within the angular range of total reflection.

Guided by these observations, we performed experiments with two liquids, methanol and isopropanol, with conditions so chosen that there was oscillatory decay for one liquid (methanol) and overdamped decay for the other.

To eliminate the difficult problem of surface contamination, the liquid samples were prepared by repeated distillation for several days into one side of an evacuated, sealed, double flask. The incident beam (from a stabilized single-mode helium-neon laser at 6328 Å) was totally reflected from the liquid surface and the scattered light, observed at an angle (θ, φ),

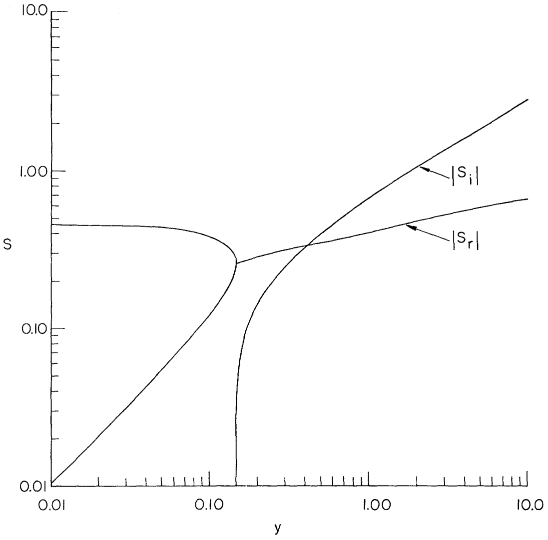

FIG. 1. Solution for the time dependence of surface waves of the form $\exp(iKx)\exp(St/\tau_0)$. $y=\sigma\rho\Lambda/8\pi\mu^2$, $\tau_0=\rho/2\mu K^2$.

was analyzed with a 10-cm flat-mirror Fabry-Perot interferometer, having a half-intensity width of ~27 MHz. The interferometer was pressure-scanned either by a slow-leak system or by a mechanically driven piston. The detector, a photomultiplier tube with a pulse-discrimination system, permitted observation of light levels as low as 1 photoelectron/sec with a room-temperature dark counting rate of approximately 2 photoelectrons/sec.

For the light scattered in the direction (θ, φ), the frequency separation between the lines in the Brillouin doublet is $\mathrm{Im}S/\pi\tau_0$; the width of each line is $\mathrm{Re}S/\pi\tau_0$, and the corresponding surface wavelength Λ, which is responsible for this scattering, is given by

$$\Lambda = (\lambda/n)(\sin^2\theta + \sin^2\theta_0 - 2\sin\theta\sin\theta_0\cos\varphi)^{-1/2},$$

where n is the index of refraction, λ is the free-space light wavelength, and θ_0 is the polar angle of the incident light beam.

With $\varphi = 50°$, $\theta = 70°$, and $\theta_0 = 80°$, we find $\Lambda = 1.25\lambda/n$, $y_{\text{methanol}} \simeq 1.18$, and $y_{\text{isoprop.}} \simeq 0.071$, with the use of the shear-viscosity data of Nozdrev.[7] The corresponding expected separation of the Brillouin lines for methanol is 42 MHz, each line having a width of 23 MHz. For isopropanol, a doublet is not expected $(y < 0.145)$, but we get two unshifted lines of widths 18 and 81 MHz, whose peak intensities are in inverse proportion to their widths. Thus, the total spectrum "width" (including the Brillouin doublet) is expected to be considerably larger for methanol than for isopropanol.

The actual measured spectral profile is complicated by the presence of extraneous unshifted light, consisting primarily of Rayleigh light scattered in the bulk of the fluid just below the surface. This extraneous light contributes approximately one-half of the observed intensity at the peak of the spectral profile, and prevents resolution of the expected Brillouin splitting in methanol. Thus only line broadenings were observed.

In Fig. 2(a), a corresponding typical measured spectral profile is compared with the calculated value. The calculated points were obtained by convolving the instrument response function with the expected spectral profile of surface-scattered light and bulk-scattered Rayleigh light. Note that the width of the surface-scattered light for isopropanol, Fig. 2(b), is noticeably smaller than for the less viscous methanol. This reduction in width can be explained by the absence of a Brillouin splitting in isopropanol. The observed difference in widths is in fair agreement with the predictions of the surface-wave theory outlined above, and supports the hypothesis that the observed scattering is caused by surface waves.

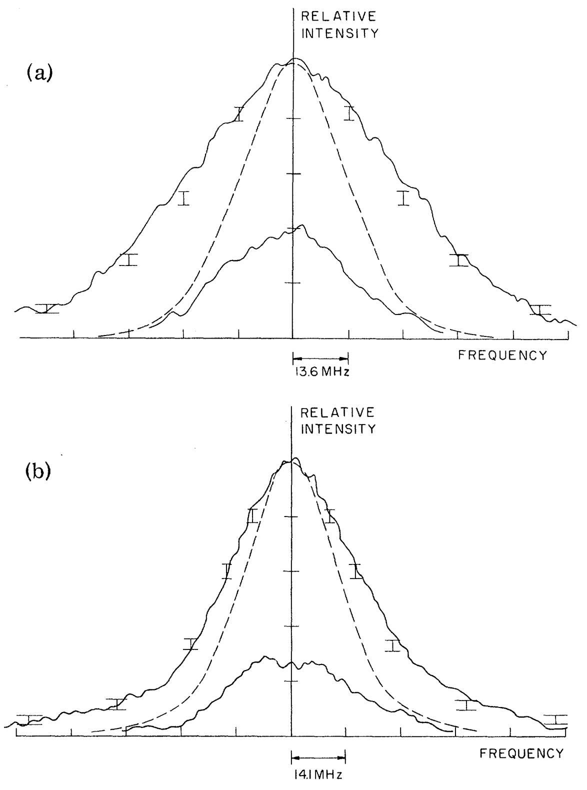

FIG. 2. (a) Results for methanol. (b) Results for isopropanol. Upper solid curve is surface-scattered light; lower solid curve is Rayleigh scattering in bulk of fluid near surface; points (I) indicate calculated value of surface plus bulk scattering convolved with instrument response; dashed curve is instrument response. The measured peak intensity for the surface scattering in both liquids is approximately 30 photoelectrons/sec, using a 0.1-mW laser. Data were taken at approximately 25°C.

With the apparatus described here improvements sufficient to resolve the expected Brillouin doublet are not feasible. But at smaller scattering angles both the surface-scattered intensity and spectral power density are much greater, and an optical-heterodyne technique should permit the resolution of the doublet.[8] This type of experiment, exploring the region of $y \simeq 25$, is now in progress.

Although the interpretation of the surface scattering given here seems to explain the observed line broadening, there exists in polar or associated liquids the possibility of structural changes near the liquid surface for depths up to several thousand angstroms.[9,10] While this effect does not seem to be important in the liquids studied, it cannot be simply dismissed on the basis of present experimental evidence. Thus, higher resolution experiments are needed for a completely conclusive interpretation of the surface scattering.

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LANDAU LEVELS AND MAGNETO-OPTIC EFFECTS AT SADDLE POINTS

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We give a quantum-mechanical treatment for the eigenstates of electrons near saddle points of the energy bands in the presence of a constant magnetic field. We find that Landau-type levels exist depending on the orientation of the magnetic field. Correspondingly, we find peaks in the interband transition probabilities and discuss selection rules on the Landau quantum numbers. We show the behavior of the optical constants for a chosen direction of the magnetic field, and indicate experimental consequences.

The quantum effects produced by a magnetic field near minima or maxima of energy bands have been studied extensively.[1-3] It has been shown that Landau levels are produced by the magnetic field and singularities in the interband transition probabilities are produced accordingly. This gives rise to magneto-optic effects corresponding to M_0 transitions between maxima of the valence band and minima of the conduction band.[4-6] A general theory of the magnetic quantum states for arbitrary shape of the energy bands has been given by Lifshitz[7] in the semiclassical limit.

We consider nondegenerate bands and expand the energy as follows, taking the origin at the saddle point:

$$E(k) = E_0 + \alpha_x \hbar^2 k_x^{\,2} + \alpha_y \hbar^2 k_y^{\,2} + \alpha_z \hbar^2 k_z^{\,2}. \tag{1}$$

We choose the axes in such a way that α_x and α_y have sign opposite to α_z. Following the procedure of Luttinger and Kohn,[8] we obtain the energy values in presence of a magnetic field, by solving the equation

$$\{\alpha_x[p_x - (e/c)A_x]^2 + \alpha_y[p_y - (e/c)A_y]^2 + \alpha_z[p_z - (e/c)A_z]^2\}F(\vec{r}) = (E - E_0)F(\vec{r}), \tag{2}$$

where $\vec{p}$ is the operator $-i\hbar\nabla$ and $\vec{A}$ is the vector potential. The wave functions are given in zero order by

$$\psi(\vec{r}, \vec{H}) = F(\vec{r})\psi(\vec{r}, \vec{k}_0), \tag{2'}$$

$\psi(\vec{r}, \vec{k}_0)$ being the Bloch function at $\vec{k}_0$. For our purposes we choose a gauge where the vector