

FOURIER TRANSFORM HETERODYNE SPECTROSCOPY OF LIQUID INTERFACES

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By acousto-optically shifting the local oscillator in a heterodyne set-up, a spectral resolution of better than 150 mHz can be obtained. Applications of the technique to the study of interfacial phenomena are discussed.

Recently there has been much renewed interest in the behavior of liquid interfaces far from the critical point. This is in part because of practical applications in industry, and in part because of recent theoretical interest in the description of liquids out of equilibrium.^{1,2} Laser light scattering has been used from the early days of the laser to study properties of liquid interfaces both far away and close to the critical point.^{3,4} By detecting the beating signal between the scattered laser light and a 'local oscillator' derived from the same laser, resolving powers of 10^{15} have been achieved. We present here recent results obtained with a novel Fourier transform heterodyne technique.^{5,6}

A detailed description of the experimental setup can be found in previous publications.^{5,6} In short, a multimode 4 mW He-Ne laser beam is incident on a liquid-vapor or liquid-liquid interface, and the inelastic and quasi-elastic scattered light is detected by optical heterodyning.^{3,4} In a conventional heterodyne setup, because the up-shifted and down-shifted components of the inelastic scattered light beat at the same frequency with the incident beam, one cannot distinguish between the two components. In the present setup, to resolve these two components, the local oscillator is frequency-shifted by acousto-optic modulation.^{5,6} The spectrum is obtained by performing a fast Fourier transform of the detected beating signal. The technique has a spectral resolution of better than 150 mHz, and a high signal-to-noise ratio. It therefore allows accurate measurement of quasi-elastically scattered light.

During the past year we have applied this technique to study various interfacial phenomena. First, we have studied the effect of a temperature gradient on surface phonons, also known as capillary waves or ripplons, on liquid-vapor interfaces.⁷ Figure 1 shows the fully resolved spectrum of the scattered light from the liquid-vapor interface of water. The unshifted central peak, appearing at the

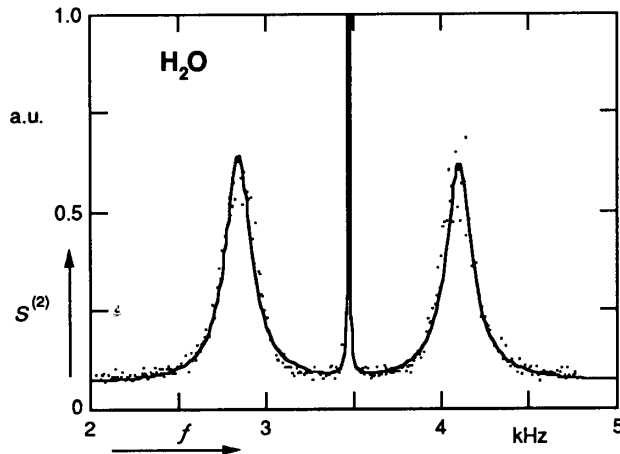


Fig. 1. Fully resolved spectrum of light scattered from the liquid-vapor interface of water at room temperature.

frequency shift of the local oscillator, is due to stray light scattering at the window of the cell, while the two symmetrically shifted side peaks (Brillouin peaks) are due to capillary waves on the surface of the liquid. An asymmetry in the height of the Brillouin peaks was predicted to occur when light is scattered from nonequilibrium bulk liquids; this was verified experimentally a few years ago.^{8,9} A recent theoretical paper predicts a similar asymmetry in the spectrum of light scattered from a nonequilibrium interface because of broken time-reversal symmetry.¹⁰ With the above setup, for the first time, we observed and measured this asymmetry in the Brillouin spectrum of light scattered from a liquid interface subject to a temperature gradient.⁷ A detailed report will appear in a forthcoming publication.

The present technique can also be applied to determine accurate values for the interfacial tension of liquid-liquid interfaces. Interfacial tension measurements are usually carried out using ellipsometric techniques or the pendant-drop method.¹¹ The interfacial tension, however, also plays a role in the dispersion of capillary waves. By studying the laser light scattering from the interface under various incident angles, one can measure the dispersion of the capillary waves on the interface, and thus experimentally determine a value for the interfacial tension.¹² Measurements were carried out on cyclohexane-methanol and water-ether, yielding accurate values for the interfacial tension for these systems. The advantages of this technique are that the interface is not disturbed, and that one can measure much lower interfacial tensions than previously possible.

Finally, the technique is also well suited to study quasi-elastic scattering from impurities and surfactants at liquid interfaces. Although it was predicted more than ten years ago that impurities at a

fluid interface modify the spectrum of scattered light,¹³ to date no optical experiments have been performed on such systems. With conventional heterodyne techniques, the central peak is always located at the origin; the $1/f$ noise makes it difficult and unreliable to analyze such a central peak. With the present technique, however, the central peak is shifted away from the origin, making a quantitative analysis of this peak possible. Figure 2a and 2b show the quasi-elastic scattering spectra from interfaces with 50 nm and 1 μm particles, respectively; the spectrum of a clean interface consists of a single narrow peak.

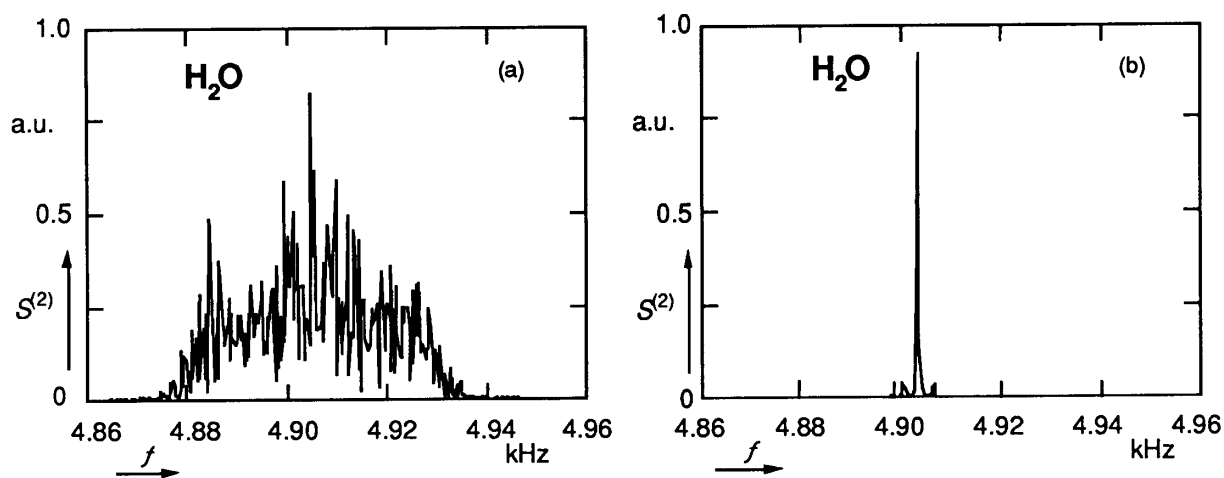


Fig. 2. Spectrum of light scattered quasi-elastically from the liquid-vapor interface of water at room temperature with (a) 50 nm particles; (b) 1 μm particles.

We have presented here a simple, convenient heterodyne technique with high resolution. Its ability to provide directional separation of the Brillouin doublet makes it suitable for the study of nonequilibrium phenomena. Due to its high sensitivity, the Fourier transform heterodyne technique also shows promise as a powerful tool to study interfacial tension, and the effects of interfacial impurities and surfactant layers.

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