A High-Performance and Simplified Quasi-Elastic Laser Scattering Method Using Homodyne Detection in Beam Divergence

ARTICLE *in* ANALYTICAL CHEMISTRY · JUNE 2001

Impact Factor: 5.64 · DOI: 10.1021/ac001338e · Source: PubMed

2 AUTHORS, INCLUDING:

Isao Tsuyumoto
Kanazawa Institute of Technology

Anal. Chem. **2001,** *73,* 2366−2368

Technical Notes

A High-Performance and Simplified Quasi-Elastic Laser Scattering Method Using Homodyne Detection in Beam Divergence

Isao Tsuyumoto* and Hiroshi Uchikawa

Department of Environmental Systems Engineering, Kanazawa Institute of Technology, 7-1 Ohgigaoka, Nonoichi, Ishikawa 921-8501, Japan

We devise the new principle of the quasi-elastic laser scattering (QELS) method using a homodyne detection technique in a beam divergence and successfully facilitate the equipment. The QELS method is a unique technique for the noncontact and time-resolved study of surface tension at liquid surfaces and liquid/liquid interfaces. The conventional QELS method requires a precise optical alignment using a local oscillator such as a diffraction grating, and the determination of the surface tension accompanies much difficulty because of the low S/N ratio of the power spectra. Our new principle allows high-performance QELS measurements by only a simple alignment of a downsized experimental setup. The power spectra are obtained with 50−100 times higher S/N ratios than the conventional ones. The power spectra are analyzed by a new theory, and the calculated surface tensions agree with the literature values. The accuracy of the surface tension measurements using the QELS method is substantially improved.

Surface tension measurements provide much information on surfactant dynamics at liquid surfaces and liquid/liquid interfaces. Common industrial processes such as washing, printing, and coating are closely related to the adsorption of surfactants, and surface tension measurements are widely used for quality control, research, and development in various industries. The measurements are also helpful for fundamental studies in view of the interfacial thermodynamics, properties, and structures. A number of methods for surface tension measurements such as the Wilhelmy method, the Du Noüy method, the spinning drop method have been reported so far,[1] but these methods bring about mechanical perturbation and are not suitable for time-resolved measurements. Katyl and Ingard reported a quasi-elastic laser scattering from liquid surfaces by capillary waves (ripplons), which are spontaneously generated at liquid surfaces.[2] Several researchers reported that the QELS method is an appropriate method for surface tension measurements, indicating that the surface tensions calculated from the capillary wave frequencies agreed with the other methods.[3−5] Tsuyumoto and co-workers have fabricated the conventional QELS measurement system based on a laser heterodyne apparatus[6] using a diffraction grating as a local oscillator and have reported on the dynamics of mass transfer of surfactants at the water/nitrobenzene interface.[7−11] However, many experimental difficulties arose in the measurements, e.g., the detection of the signal from the capillary waves was very difficult because of the extremely small amplitude of the waves (∼10 nm), and the determination of the surface tensions included accidental errors due to the low S/N ratio of the observed power spectra. In this study, to improve the QELS method, we devise a homodyne detection technique using a beam divergence instead of heterodyne detection using the diffraction grating. We present here the measurement results of standard samples and discuss the advantages of the new homodyne QELS method.

PRINCIPLE

The principles of the conventional and the new homodyne QELS methods are shown in Figure 1a and b, respectively. A thermally generated spontaneous density fluctuation occurs at the liquid surface. The surface tension acts as a restoring force on the fluctuation, and it excites a surface tension wave, which is called a capillary wave or ripplon. The capillary waves occurring on liquid surfaces have various wavelengths, and each frequency is dependent on each wavelength. This makes it essential to select a capillary wave with a certain wavelength to determine the dispersion relation of the waves. The QELS methods measure the

(1) Mingins, J.; Taylor, J. A. G.; Pethica, B. A.; Jackson, C. M.; Yue, B. Y. T. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 323.
(2) Katyl, R. H.; Ingard, U. *Phys. Rev. Lett.* **1968**, *20*, 248.
(3) Sakai, K.; Tanaka, H.; Takagi, K. *Jpn. J. Appl. Phys.* **1990**, *29*, L2247.
(4) Sauer, B. B.; Chen, Y. L.; Zografi, G.; Yu, H. *Langmuir* **1988**, *4*, 111.
(5) Sano, M.; Kawaguchi, M.; Chen, Y.-L.; Skarlupka, R. J.; Cheng, T.; Zografi, G.; Yu, H. *Rev. Sci. Instrum.* **1986**, *57*, 1158.
(6) Härd, S.; Hamnerius, Y.; Nilsson, O. *J. Appl. Phys.* **1976**, *47*, 2433.
(7) Uchiyama, Y.; Tsuyumoto, I.; Kitamori, T.; Sawada, T. *J. Phys. Chem. B* **1999**, *103*, 4663.
(8) Uchiyama, Y.; Kitamori, T.; Sawada, T.; Tsuyumoto, I. *Langmuir* **2000**, *16*, 6597.
(9) Uchiyama, Y.; Fujinami, M.; Sawada, T.; Tsuyumoto, I. *J. Phys. Chem. B* **2000**, *104*, 4699.
(10) Zhang, Z. H.; Tsuyumoto, I.; Kitamori, T.; Sawada, T. *J. Phys. Chem. B* **1998**, *102*, 10284.
(11) Zhang, Z. H.; Tsuyumoto, I.; Takahashi, S.; Kitamori, T.; Sawada, T. *J. Phys. Chem. A* **1997**, *101*, 4163.

10.1021/ac001338e CCC: $20.00
Published on Web 04/05/2001

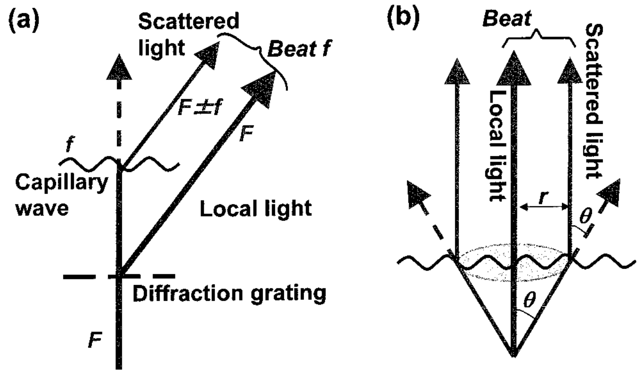

Figure 1. Measurement principles of the QELS methods. (a) The conventional heterodyne technique using a diffraction grating and (b) the new homodyne technique utilizing a beam divergence.

capillary wave frequency of a selected wavelength, and the surface tension is calculated from the relationship between the frequency and the wavelength. The two principles are different in the technique for selecting the wavelength and for measuring the frequency.

(a) The Conventional Heterodyne QELS. A brief outline of the principle of the conventional method based on Figure 1a follows. The incident beam normal to the surface is quasi-elastically scattered by the capillary wave with a Doppler shift at an angle determined by the following equation:

$$K \tan \theta = k \tag{1}$$

where K and k are the wavenumbers of the incident beam and the capillary wave, respectively. Thus, the wavenumber k of the capillary wave is obtained by giving θ. To adjust the angle θ, a transmitting diffraction grating was arranged in front of the cell. The angle θ is determined by the following equation using the spacing d and the order n of the diffraction grating,

$$d \sin \theta = n\lambda \tag{2}$$

where λ is the wavelength of the laser beam. From eqs 1 and 2, the wavenumber k and the wavelength Λ of the observed capillary wave are obtained.

The capillary wave frequency is detected by an optical heterodyne technique, which uses a diffracted beam as a local light. The incident laser beam (F Hz: $F = c/\lambda$) is quasi-elastically scattered by the capillary wave (f Hz) at the liquid surface. The scattered beam is accompanied by a Doppler shift, and its frequency becomes $F \pm f$ Hz. The scattered beam ($F \pm f$ Hz) is optically mixed with the diffracted beam (F Hz) from the diffraction grating to generate an optical beat in the mixed light. The beat frequency (f Hz) obtained here is the same as the Doppler shift, i.e., the capillary wave frequency.

In the measurement, by locating a photodiode at the nth diffraction spot, the power spectrum of the capillary wave with the wavelength calculated from eqs 1 and 2 is obtained. The S/N ratio of the power spectrum depends on the beat intensity in the mixed light, and the beat intensity is proportional to the product of the electric field intensities of the scattered light and the diffracted light. The intensity of the diffracted light is not more than 5% of the light source, and the observed scattered light is only a small portion (~1%) of the expedient light scattered in the shape of concentric circles. These result in the low S/N ratio of the spectra, and a precise optical alignment is necessary because of the experimental difficulties in detecting the signals.

(b) The New Homodyne QELS. To improve the disadvantages of the conventional QELS method, we devised a principle using homodyne detection technique in a beam divergence as shown in Figure 1b. A laser beam with a continuous intensity distribution in the divergence is incident normal to the surface. The light intensity has a maximum at the center of the irradiated spot and decreases monotonically with the distance from the center. Because of the divergence, the angle of incidence varies as a function of the distance from the center. The strongest part of the beam is incident exactly normal to the surface, and its transmitted light is used as a local light (F Hz). The surrounding parts of the beam are incident obliquely and are scattered almost nondirectionally by capillary waves of various wavelengths. Some parts of the light are scattered exactly normal to the surface with a scattering angle of θ and are mixed with the local light to generate an optical beat. By locating a photodiode at the strongest part of the transmitted light, the optical beat between the local light and the scattered light is observed in a power spectrum. Because of the continuous spatial distribution of the incident beam, the scattered beam generating the optical beat consists of multiple scattering angles. The scattering angle that generates the greatest signal intensity can be determined from the angle of the beam divergence and it gives the wavelength of the observed capillary wave as follows. The relationship between this wavelength and the observed peak frequency gives a surface tension.

The electric field intensity of the incident beam at a distance of r from the center is expressed by the following equation,

$$E(r) \propto \exp(-r^2/a^2) \tag{3}$$

where a is the spot radius whose intensity is $1/e^2$ of the center. While the electric field intensity $E(r)$ decreases monotonically with increasing r, the scattering area of the same scattering angle θ increases in proportion to a circle with radius r, i.e., $2\pi r$. Thus, the electric field intensity generated by all the scattered light at a distance of r from the center is approximately expressed by the following equation,

$$E(r) \propto 2\pi r \exp(-r^2/a^2) \tag{4}$$

The relative maximum of this equation corresponds to the peak frequency of the power spectra, because the beat intensity is proportional to this electric field intensity. By differentiating eq 4, we find the maximum at $r = a/\sqrt{2}$. This corresponds to the scattering angle of $\theta_0/\sqrt{2}$, where θ_0 is the beam divergence of the light source. By substituting the angle of $\theta_0/\sqrt{2}$ into eq 1, we can obtain the wavelength of the capillary wave corresponding to the peak in the power spectrum. In the present study, the beam divergence of the light source is 1 mrad, and thus the wavelength of the observed capillary wave is calculated as 0.752 mm.

The surface tension γ is calculated from the relationship between the capillary wave frequency f and the capillary wave wavenumber k using Lamb's equation,

$$f = (1/2\pi)(\gamma/\rho)^{1/2}k^{3/2} \tag{5}$$

where ρ is the density of the liquid and k is the wavenumber of the capillary wave.

EXPERIMENTAL SECTION

Apparatus. The experimental setup of the new homodyne QELS method is shown in Figure 2. It is much facilitated and downsized compared to the conventional one, because the beam divergence is already inherent in a compact laser light source and the diffraction grating is unnecessary. The beam from a diode-pumped YAG laser (CrystaLaser, model GCL-025S, 532 nm, 25 mW) is incident normal to the liquid surface after passing through the bottom of the sample cell. An aperture (1 mm diameter) is located at the strongest part of the transmitted light, and the selected light is detected by a photodiode (Hamamatsu Photonics S1290). Signals from the photodiode are Fourier transformed and saved by a personal computer.

Reagents. Ethanol (Kanto Chemical Co., Inc.; special grade; 99.5%), acetone (Kanto Chemical Co., Inc.; special grade; 99.5%), and distilled water were used as samples. Measurements were performed at 22 °C.

RESULTS AND DISCUSSION

A power spectrum for capillary waves at an ethanol surface is shown in Figure 3. The spectrum is obtained with 50−100 times higher intensity and S/N ratio than the conventional methods in our previous papers.[9−11] The peak appearing at 0.64 kHz is the beat frequency, i.e., the capillary wave frequency with the wavelength of 0.752 mm, as we discussed above. The second, third, and fourth harmonics are also observed around 1.4−2.6 kHz, along with the fundamental wave at 0.64 kHz. The surface tension was calculated from the fundamental capillary wave frequency of 0.64 kHz. Substituting the frequency, the wavelength, and the density into eq 5, the surface tension of ethanol at 22 °C was calculated as 21.8 mN/m. This is in agreement with the literature value of 22.3 mN/m.[12] As shown in Table 1, the peak frequencies of the fundamental waves for acetone and water were observed at 0.65 and 1.03 kHz, respectively. The calculated surface tensions were also in agreement with the literature values. It was also possible to observe the decrease in surface tensions in situ. The peaks of the water surface including the second and the third harmonics shifted to smaller frequencies by addition of surfactant. This indicates that the present QELS method can be also applied to monitor molecular dynamics at liquid surfaces and liquid/liquid interfaces.

The measurements were also performed with the reflection-type configuration. The beam was incident nearly normal to the surface and the photodiode was located at the strongest part of the reflected light. The S/N ratios and the peak frequencies were the same as those of the above transmission type. This shows that the present QELS method can also observe opaque solutions such as suspensions.

The present QELS method will be useful in the measurements of high-temperature liquids such as fused silicon, whose surface tension in the manufacturing process affects the quality of the product of semiconductor monocrystals. It will be also possible to perform microscopic measurements of surface tension, because the present principle applies to a beam convergence as well as the beam divergence. By focusing the beam in the vicinity of the surface, we can obtain the signal from microsurfaces such as in the channels of μ-TAS (micro total analysis systems). We expect that the present QELS method will contribute significantly to the development of microchemistry at liquid surfaces and liquid/liquid interfaces. Moreover, the same principle using beam divergence can be applied to the other laser scattering methods observing the Doppler shift such as Doppler current meters and zeta potentiometers. We also expect that the present principle will bring about a tremendous ripple effect to laser spectroscopy.

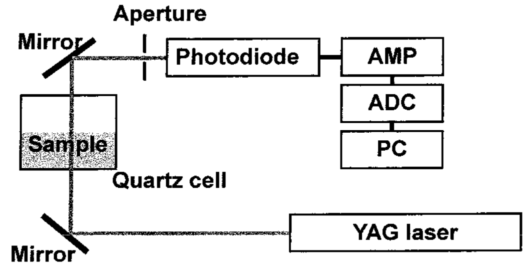

Figure 2. Schematic view of the experiment setup of the new homodyne QELS method: AMP, preamplifier; ADC, analog−digital converter; PC, personal computer.

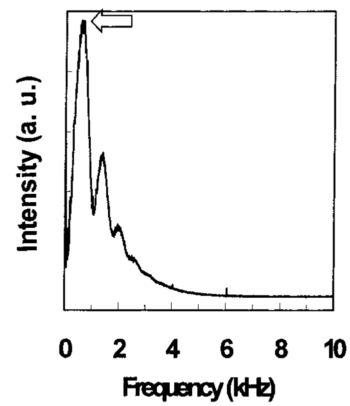

Figure 3. A typical power spectrum for capillary waves at an ethanol surface. The peak corresponding to the fundamental wavelength of 0.752 mm is marked by an arrow.

Table 1. The Peak Frequency f, the Experimental Surface Tension by the Present QELS Method γ_{obs}, and the Reported Surface Tension $\gamma_{lit.}$[12]

	f (kHz)	γ_{obs} (mN/m)	$\gamma_{lit.}$ (mN/m)
ethanol	0.64	21.8	22.3
acetone	0.65	22.6	23.8
distilled water	1.03	71.7	73.2

Received for review November 15, 2000. Accepted February 5, 2001.

AC001338E

(12) Jasper, J. J. *J. Phys. Chem. Ref. Data* **1972**, *1*, 841.