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Low Frequency Laser Debye-Sears
Ultrasonic Measurements

by

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The frequency range accessible to the laser Debye-Sears technique has been extended downward to 7 MHz. Modifications include a 1 MHz piezoelectric transducer, a 5 mW HeNe probe laser, and an extended optical path. The precision is experimentally characterized using the complexation of NaCl and 18-crown-6 in H_2O. The accessibility of lower frequencies permits the detection of a previously unobserved second relaxation.

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Low Frequency Laser Debye-Sears Ultrasonic Measurements

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ABSTRACT

The frequency range accessible to the laser Debye-Sears technique has

been extended downward to 7 MHz. Modifications include a 1 MHz

piezoelectric transducer, a 5 mW HeNe probe laser, and an extended optical

path. The precision is experimentally characterized using the complexation

of NaCl and 18-Crown-6 in H_2O. The accessibility of lower frequencies

permits the detection of a previously unobserved second relaxation.

INTRODUCTION

Ultrasonic absorption techniques cover a wide time range (10^{-5} - 10^{-10} seconds). The difficult and time consuming nature of many ultrasonic methods, and the need for more than one ultrasonic instrument to cover the desired 0.5 MHz to 500 MHz frequency range, has limited the use of ultrasonic techniques. Of the several ultrasonic methods, the laser Debye-Sears technique is perhaps the easiest and quickest to use. Eyring and coworkers[1] developed an automated system capable of measuring frequencies between 15 and 300 MHz. Automation results in shorter measurement time and higher precision than is typically obtained with pulsed systems over the same frequency range.[2]

Sound waves produce periodic variations in the density of a condensed phase which can act as a three dimensional diffraction grating for a light beam. The strength of the acoustic signal can be monitored using a laser beam diffracted by this grating. The acoustic absorption coefficient, α, is calculated from the intensity of the diffracted beam as a function of the distance between the transducer and the laser beam. The ultrasonic frequency dependence of α contains kinetic and thermodynamic information about chemical reactions occurring in the sample medium. Stuehr[2] discusses this relationship in detail.

At Utah, a 5 MHz transducer has been excited at its odd harmonics to determine α at frequencies above 15 MHz. When necessary, ultrasonic data between 1 and 15 MHz have been obtained using the resonance technique in

collaboration with other researchers.[3] This note reports an extension of the laser Debye-Sears technique to frequencies below 15 MHz. This is accomplished with a 1 MHz transducer using a HeNe laser rather than the more expensive Ar^+ laser used in previous work. Reexamination of the complexation of NaCl with 18-crown-6 in aqueous solution over a lower frequency range reveals a second relaxation which was previously undetected. The lower frequency range has also proven useful in similar rate studies of reactions in dry aprotic solvents.

I. ULTRASONIC APPARATUS

A schematic of the optical path used to separate the diffracted and undeflected beams is shown in Fig. 1. The ultrasonic path length, the angle of the laser beam relative to the transducer, and the positioning of the moveable mirror are varied using stepping motors (Superior Electric) controlled from an IBM XT-286 computer with routines written in the C language. The optical path length is 16 feet; the entire apparatus occupies 12 feet of bench top.

The transducer is an X-cut quartz crystal(Valpey-Fisher) with a fundamental frequency of 1 MHz and a diameter of one inch. The output of a Hewlett-Packard 8656B synthesized signal generator is amplitude modulated before being applied to the transducer. A PARC 124 lock-in detector measures the signal from the photomultiplier.

A 5 mW HeNe laser (CW Radiation) monitored the acoustic strength, in contrast to a 200 mW Ar^+ laser used previously.[1] Even with the lower laser

power, the diffracted beam required attenuation before detection. (For example, at 9 MHz the beam was attenuated by a factor of 20). With this arrangement, α has been measured at frequencies up to 71 MHz.

II. REAGENTS

Sodium chloride (Mallinckrodt) was dried at 70°C before use. 18-Crown-6 (Parish) was purified using standard methods.[4] Solutions were prepared with deionized water.

III. RESULTS AND DISCUSSION

The precision of low frequency results has been evaluated using an aqueous solution of 0.30 M NaCl and 0.096 M 18-crown-6 at 25°C. The intensity of the diffracted light as a function of the ultrasonic path length is

$$I(x) = I(0) \exp(-2\alpha x) \tag{1}$$

Here x is the ultrasonic path length in centimeters, α is the acoustic absorption coefficient (in cm^{-1}), and I(x) is the intensity of the diffracted beam. Estimates of α, denoted $\hat{\alpha}$, and its standard deviation, denoted $s(\hat{\alpha})$, are calculated from the slope of a linear regression of the logarithm of I(x) versus x. Measurement errors in the light intensity and transducer position, as well as deviations from a straight line relationship are included in $s(\hat{\alpha})$. Consequently, the relative standard deviation, $s(\hat{\alpha})/\hat{\alpha}$, reflects the overall precision in $\hat{\alpha}$. The average percentage

relative standard deviation at several frequencies is shown in Table I. Also listed are the mean values of α at these frequencies and the mean deviation between replicate measurements as a percentage of the mean. For a small number of observations, the mean deviation performs better than the root mean square deviation. Both measures of precision in Table I demonstrate the reliability of this method at low frequencies.

The complexation of NaCl with 18-crown-6 in aqueous solution has previously been studied[5] using the Debye-Sears technique at frequencies above 15 MHz. Results on a solution containing 0.30 M NaCl and 0.096 M 18-crown-6 revealed a single relaxation at 15.2 MHz. In the absence of a resonator cell, examination of lower frequencies was not then possible. Additional laser Debye-Sears data have now been obtained under identical conditions using a 1 MHz quartz transducer. Figure 2 presents the combined laser Debye-Sears data from a 5 MHz crystal and a 1 MHz crystal. Analysis of the data in Fig. 2 using a nonlinear least squares algorithm reveals the presence of two relaxations at 11.2 MHz and 28 MHz. The data have been plotted as excess absorption to emphasize low frequencies. Similar conclusions are reached from the analysis of Debye curves.[2]

Eliminating the need for an ultrasonic resonator for all but the very lowest frequencies is not the only potential benefit of this work. The Debye-Sears method gives a direct measure of α. The resonator method, on the other hand, requires correction terms for mechanical loss, and can produce systematic errors.[6,7] The Debye-Sears method is not suitable for solutions of low absorption, such as pure water. Such cases are easily

recognized by a large value of $\hat{s}(\alpha)$, and can be avoided. However, this is not usually a problem in the study of kinetic processes.

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FOOTNOTES AND REFERENCES

a) Currently an NRC Postdoctoral Research Associate. Ballistic Research Laboratory, Aberdeen Proving Ground, Maryland 21005-5066.

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Table I. Precision of α versus Frequency

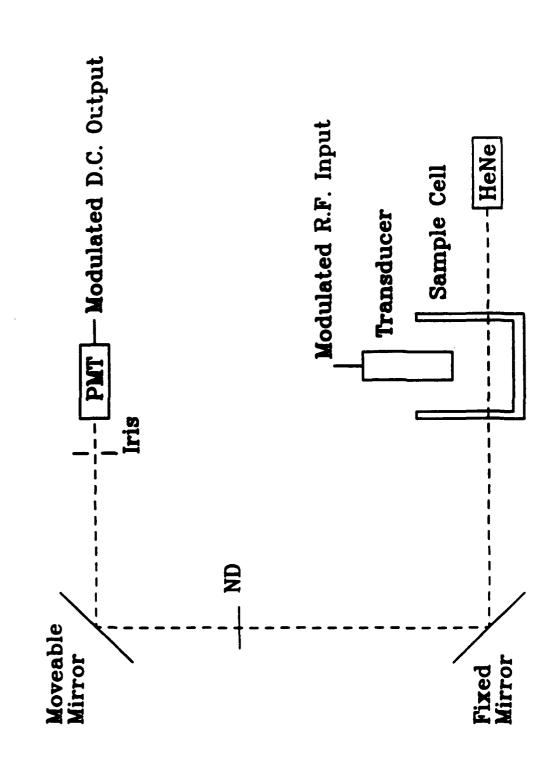| f, MHz	$\bar{\alpha}$, cm^{-1}[a]	RSD,[b] %	RMD,[c] %
7.	0.178	3.8	2.6
9.	0.253	0.7	3.0
11.	0.344	0.8	0.3
13.	0.430	0.8	1.2
15.	0.489	0.8	0.9
17.	0.520	0.9	2.2
19.	0.571	0.6	0.8
21.	0.646	0.7	0.7
23.	0.715	1.0	0.4

[a] Average of 3 - 5 replicate measurements at each frequency.

[b] Relative Standard Deviation. RSD = $(100\%/n) \cdot \Sigma_i \, s(\hat{\alpha}_i)/\hat{\alpha}_i$, where the summation is over n replicate measurements.

[c] Relative Mean Deviation. RMD = $(100\%/n) \cdot \Sigma_i \, \{|\alpha_i - \bar{\alpha}|/\bar{\alpha}\}$.

Figure Captions

Figure 1. Schematic diagram of the optical path used to separate the
diffracted and undeflected beams. Neutral density filters are
symbolized by ND. For clarity, no connections with the XT
computer are shown.

Figure 2. Plot of $\alpha\lambda$ as a function of ultrasonic frequency, where λ is
the wavelength of sound in solution. Measurements using a 1
MHz transducer(o) are consistent with those using a 5 MHz
transducer(Δ) from reference 5. The solid line is the sum of
two relaxations.

Frequency, MHz