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Possible applications of surface electromagnetic waves to measure absorption coefficients*

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We show that surface electromagnetic waves can probably be used to measure the absorption coefficients of materials overlaying metals. The proposed experimental method is illustrated in the infrared frequency range using water, Teflon, and polyethylene as sample materials.

I. INTRODUCTION

We suggest an application of surface electromagnetic (SEM) waves¹⁻³ to measure the optical constants of materials which *cannot* propagate SEM waves themselves. The sample need only be a thin layer upon a gold or other metal surface. To measure the optical properties of the sample, the propagation distances of the SEM waves are measured, and using the results of Bell *et al.*,⁴ the optical constants of the sample can be determined. The method promises to be quite sensitive and may be particularly useful even for samples of monolayer thickness. In what follows, we present details of the method and the necessary theoretical results and then give some illustrative calculations.

II. THE METHOD

The propagation distance, L_x , of SEM waves is measured in a rather direct fashion using two prisms as illustrated in Fig. 1. The first prism serves to launch an SEM wave (surface plasmon here) in the metal substrate upon which the sample has been placed as a layer. The second prism couples the energy out of the surface wave. By measuring the energy coupled out as a function of prism separation, D , the $1/e$ propagation distance of the SEM wave may be determined.⁵

We assume the SEM wave is propagating in the $+x$ direction, the z direction is normal to the sample-metal interface, the complex dielectric constant of the sample is $\eta \equiv \eta_1 + i\eta_2$, and the dielectric constant of the metal substrate is $\epsilon \equiv \epsilon_1 + i\epsilon_2$. We shall assume $\epsilon_1 < -\eta_1$ in the frequency region of interest so that surface plasmons exist at the sample-metal interface. The prism will be assumed to be nonabsorbing and to have an index of refraction n_p .

The condition for exciting surface plasmons with

radiation of wavenumber σ incident upon the prism base with an angle θ is⁴

$$n_p \sin \theta = \text{Re} \left\{ \epsilon(\sigma) \eta(\sigma) / [\epsilon(\sigma) + \eta(\sigma)] \right\}^{1/2}. \quad (1)$$

For surface plasmons this reduces to

$$n_p \sin \theta \approx [\eta_1(\sigma)]^{1/2} \quad (2)$$

as long as σ is not too close to the surface plasmon frequency, since $|\epsilon_1(\sigma)| \gg \eta_1(\sigma)$. This means excitation of the surface plasmon requires θ equal to the critical angle. The imaginary part of the x -component of the wave vector (i. e., k_{2x}) determines the propagation distance $L_x \equiv 1/k_{2x}$. The general expression⁴ for L_x is rather complicated; so, we give here an approximation, namely

$$L_x \approx [1/(2\pi\sigma)] [\eta_1^{1/2} \epsilon_1^2 / (\eta_2 \epsilon_1^2 + \epsilon_2 \eta_1^2)]. \quad (3)$$

This approximation is valid for $|\epsilon_1| \gg \eta_1$. If the sample has a reasonable absorption, then $\epsilon_2 \eta_1^2$ usually can be neglected compared to $\eta_2 \epsilon_1^2$, and we find the simple relation

$$L_x \approx 1/\alpha, \quad (4)$$

where α is the absorption coefficient of the overlayer sample.

Figure 2 shows L_x for surface plasmons on gold.⁶ Below 5000 cm^{-1} , L_x is large enough (greater than 1 mm) to be useful for this method. Also shown on the same figure is L_x for a gold substrate with a

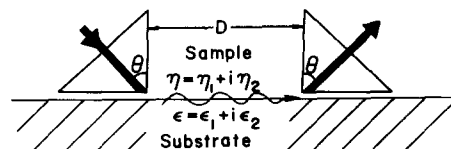


FIG. 1. Schematic diagram of method to measure L_x .

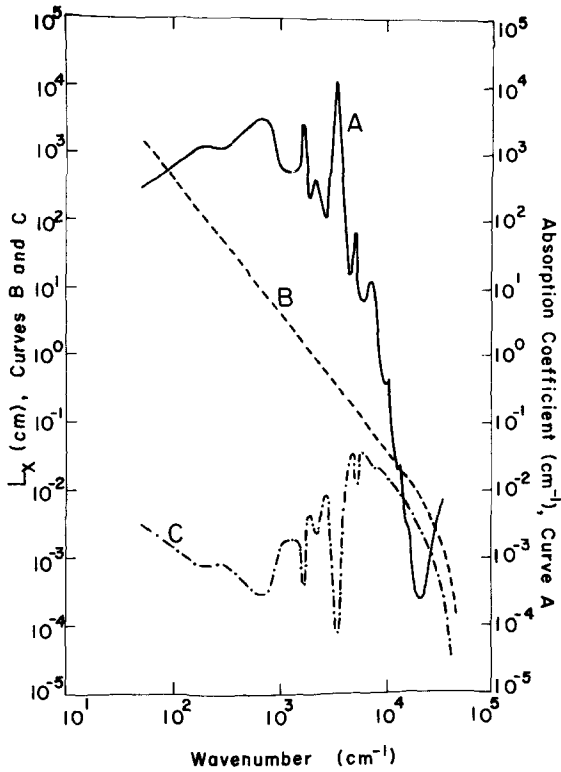


FIG. 2. Curve A shows the absorption coefficient for water; curve B shows L_x for surface plasmons on gold with a vacuum overlayer; curve C shows L_x for surface plasmons on gold with a water overlayer.

water overlayer. Note that below 5000 cm^{-1} , the relation $L_x = 1/\alpha$ holds to within one percent. Above this frequency $\epsilon_2 \eta_1^2$ can no longer be neglected and Eq. (3) must be used.

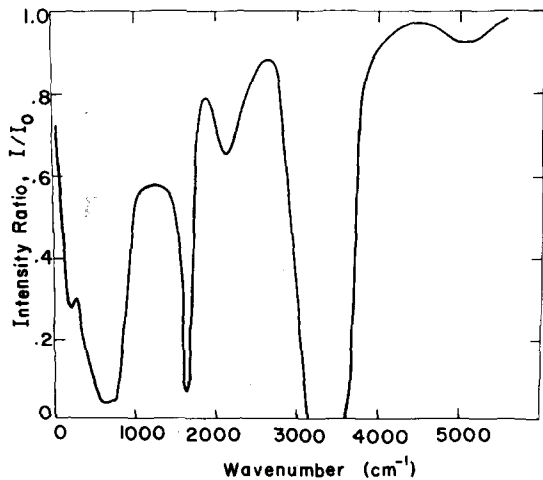


FIG. 3. Calculated transmission ratio for surface plasmons on gold with a water overlayer as a function of frequency. Prism separation is $10 \mu\text{m}$.

III. SOME EXAMPLES

As a sample calculation, we have chosen water and used the data for the optical constants of water from the compilation of Hale and Query.⁷ We shall consider a thick layer of water and a monolayer of water, both upon a gold substrate. We first discuss the "thick" water overlayer.

For water on a gold substrate, the inequality $\epsilon_2 \eta_1^2 \ll \eta_2 \epsilon_1^2$ holds (to one percent) for frequencies below 5000 cm^{-1} . Figure 3 shows the ratio ("transmission ratio") of the intensity received at the second prism with the water overlayer (I) to the intensity received when there is a vacuum overlayer (I_0). The prism separation is $10 \mu\text{m}$. This ratio is identical to the transmission through a $10 \mu\text{m}$ thickness of water showing that $L_x = 1/\alpha$ as it should.

This technique is of more importance when the surface itself is of interest. As a simple example, we consider a monolayer of water on a gold substrate. Experimental results⁸ indicate that monolayer coverage is about 9×10^{14} molecules per cm^2 . Assuming this value, we have calculated the "transmission ratio" for a 10-cm prism separation for a monolayer of water. To do this we set $\eta_1 = 1$ and assumed η_2 proportional to the concentration and used $9 \times 10^{14} \text{ cm}^{-3}$ as the effective concentration for the monolayer. The calculated "transmission ratio" is shown in Fig. 4. The frequency region over which this method can be used is limited by the attenuation in the gold. Above 1000 cm^{-1} , a 10-cm path difference is no longer feasible because of the absorption in the gold substrate. The intensity I_0 at 1000 cm^{-1} is 7% of that at 50 cm^{-1} due to the attenuation in the gold substrate. The

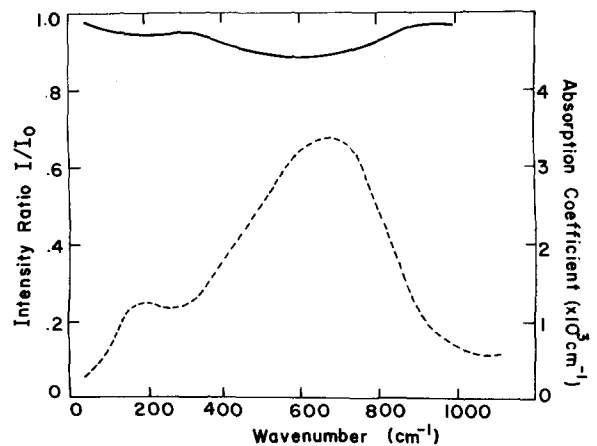


FIG. 4. Calculated transmission ratio for surface plasmons on gold with a monolayer of water as a function of frequency (solid curve). Prism separation is $10 \mu\text{m}$. Absorption coefficient of water (dashed curve).

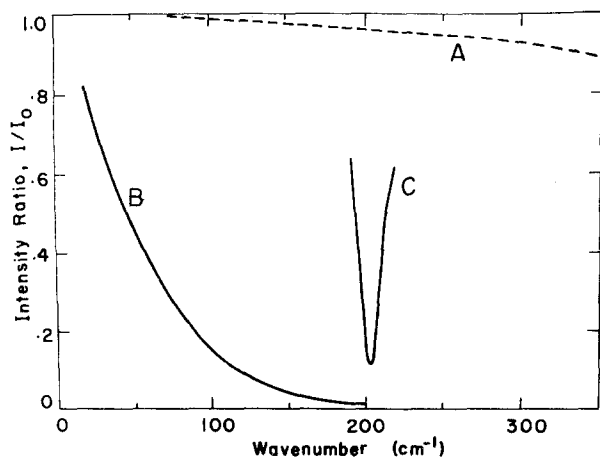


FIG. 5. Calculated transmission ratio for surface plasmons on copper with: A, polyethylene overlayer and prism separation of 1 cm; B, black polyethylene overlayer and prism separation of 0.1 cm; C, teflon overlayer and prism separation of 0.01 cm.

value of L_x , due to the increase in the electron mean-free-path, increases approximately as $1/T$ as the temperature is lowered. Thus, for low temperatures, even greater experimental sensitivity using larger effective prism separation is contemplated. Also, it should be pointed out that the absorption coefficient for an adsorbed mono-layer of water may not resemble that of bulk water too closely and this experiment would be interesting to perform.

Although the mean-free-path of surface plasmons on copper^{4,6} is less than the mean-free-path on gold, copper is also a suitable substrate. Figure 5 shows the rather weak absorption in Teflon⁹ at 200 cm^{-1} . The Teflon is coated on a copper substrate and the path length is 0.1 mm. Also shown is the transmission ratio for polyethylene¹⁰ (1-cm path length) and black polyethylene (0.1-cm path length).

IV. CONCLUSIONS

Surface plasmons on a metal-sample interface can be used to measure the absorption coefficient

of the sample. The method is particularly useful for very thin or dilute samples. It is sensitive enough that it may be useful for the study of sorbed atoms on metal surfaces.

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