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Absorption in the infrared of surface electromagnetic waves by adsorbed molecules on a copper surface*

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Experimental observations have been made for the first time that surface electromagnetic wave (SEW) spectroscopy can be used to measure the infrared spectra of adsorbed molecules and very thin films on metal surfaces. Using a tunable CO_2 laser (9.2–10.8 μm wavelength), the 975 and the 1037 cm^{-1} resonances of 5–25 Å thick physisorbed benzene on copper were observed. Broadening of these resonances for the thinnest layers of benzene was observed. Also SEW spectroscopy and ellipsometry were used to study thin films of cellulose acetate (15–75 Å) on copper. Further, it was shown that film thicknesses determined by SEW spectroscopy are in agreement with the ellipsometric thicknesses and that the SEW method is more sensitive for very thin (<25 Å) films.

I. INTRODUCTION

Surface electromagnetic waves (SEW), sometimes called surface polaritons or surface plasmons, have been extensively studied theoretically and experimentally in the last several years. The various properties of these surface excitations are described in several review papers.[1–5] Recently, theoretical calculations by Bell *et al.*,[1] have demonstrated the possibility of using various properties of SEW to investigate adsorbed molecules on metal surfaces. They suggested that SEW spectroscopy could be used to obtain the infrared spectra of adsorbed molecules on a metal surface.

In this paper, the first experimental studies of the SEW spectra of attached molecules on a metal surface are presented for physisorbed benzene and water on copper surfaces at low temperatures as well as for cellulose acetate on copper surfaces. By use of a tunable CO_2 laser and the two-prism technique,[6–8] the 1037 and the 975 cm^{-1} resonances of benzene for layers 5 to 25 Å thick have been observed. The data indicate benzene exists on the copper surface in the solid phase as the observed 975 cm^{-1} resonance does not appear in the gas phase. The variation in the propagation distance L_x of the SEW on copper with a thin (15 to 75 Å) cellulose acetate film has been studied near its 1050 cm^{-1} resonance.

Finally, a new technique for estimating the mean thickness of very thin films on metals has been developed. If the index of refraction of the thin film is known in a region where the absorption is small, the SEW theory relates the film thickness to the propagation distance L_x in a simple manner. For both cuprous oxide films on copper[8] and cellulose acetate films on copper, the film thicknesses as measured by SEW spectroscopy and ellipsometry were in good agreement. This method was used to estimate the mean thickness of adsorbed benzene and water layers on copper and was found sensitive to approximately a 5 Å thick layer of benzene.

II. THEORY

The propagation distance L_x is defined as the distance for the intensity of the SEW to decay by a factor of $1/e$. From the two-media dispersion relation of SEW,[9] L_{0x} for a metal–air system is

$$L_{0x}(\omega) = \omega_p^2/2\pi\omega^2\omega_\tau \ , \tag{1}$$

where ω_p and ω_τ are the plasma frequency and the electron scattering frequency, respectively. This relation is obtained by assuming a Drude model for the complex dielectric function $\epsilon(\omega)$ so that

$$\epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\omega\omega_\tau} \ , \tag{2}$$

where for copper $\epsilon_\infty \approx 1$.

For explaining our experimental results, the three-media system is defined as the metal substrate which supports the SEW, an overlying film of material which may or may not support SEW, and an air or vacuum overlayer as shown in Fig. 1.

Bell *et al.*,[1] have applied various approximations to the dispersion relations of SEW on three-media systems for which the layer between the metal and the air is very thin film with $d \ll \lambda/\sqrt{\epsilon_2'}$. Here, ϵ_2' is the real part of the dielectric constant of the film of thickness d and λ is the vacuum wavelength of the incident radiation. From Eq. (64) of Ref. 1, an approximate expression for the propagation distance in a metal–film–air system is

$$L_x = L_{0x}(1 + 2\pi\omega\Delta_2 L_{0x})^{-1} \ , \tag{3}$$

where L_{0x} is the propagation distance of SEW on the metal–air system of Eq. (1) and Δ_2 from Eq. (73) of Ref. 1 is approximately

$$\Delta_2 \approx \frac{4\pi\omega d}{\sqrt{-\epsilon_1'}} \frac{[(\epsilon_2')^2 + (\epsilon_2'')^2 - \epsilon_2']\epsilon_1''/(-2\epsilon_1') + \epsilon_2''}{(\epsilon_2' + \epsilon_2''\epsilon_1''/2\epsilon_1')^2 + (\epsilon_2'' + \epsilon_2'\epsilon_1''/2\epsilon_1')^2} \ , \tag{4}$$

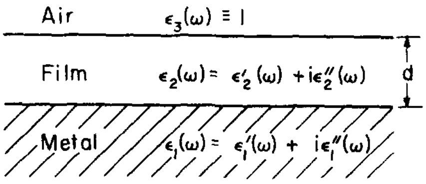

FIG. 1. Three-media system of metal, film of thickness d, and vacuum.

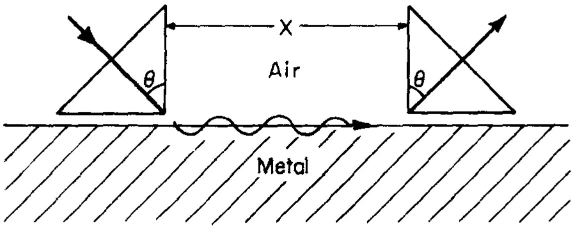

FIG. 2. Experimental arrangement for measuring the propagation distance of SEW and SEW spectra on a metal with the two-prism technique.

where $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ are the dielectric constants of the metal and film, respectively. Single primes designate the real parts and double primes the imaginary parts.

The two-prism technique is employed to measure L_{0x} and L_x. By fixing the distance x between the prisms and measuring the SEW signals $I(\omega, x)$ and $I_0(\omega, x)$, the SEW transmission spectra for metal–overlayer–air systems can be obtained from

$$T \equiv I(\omega, x)/I_0(\omega, x) = \exp[-x(1/L_x - 1/L_{0x})] , \qquad (5)$$

where $I_0(\omega, x)$ is the SEW intensity measured on the bare metal surface, and $I(\omega, x)$ is the intensity measured on the metal surface with an overlayer. By substituting Eq. (3) in Eq. (5), one has

$$T(\omega, x) = \exp(-2\pi\omega\Delta_2 x). \qquad (6)$$

III. EXPERIMENTAL TECHNIQUE AND RESULTS

A. General

In the two-prism technique, the first prism is used to excite SEW and the second prism is used to decouple SEW (as shown in Fig. 2). Note that this measurement integrates the absorption by molecules on the surface between the prisms in a manner which is analogous to bulk infrared transmission studies. In an ordinary reflection measurement, the radiation traverses the film in the direction perpendicular to the film.

For most metals, $\epsilon_1(\omega)$ is large and negative at infrared frequencies. This implies that $k_{1x} \approx \omega/c$, where k_{1x} is the real part of the x component of the SEW wave vector. This means θ (Fig. 2) is very close to the critical angle θ_c of the prism. The efficient coupling of SEW on metal surfaces without large recoupling back to the prism requires a gap between the prism base and the metal surface. We have experimentally determined the gap heights for optimum coupling of SEW for various metals, and our values are roughly one-half of the calculated field extension distance into the air above the surface.[7,8]

A 20 W Molectron CO_2 laser, tunable from 9.2 to 9.7 μm and from 10.2 to 10.8 μm, was used as a source. The radiation beam was mechanically chopped at 100 Hz and then divided into two beams by a BaF_2 crystal. The reflected beam was used as a reference, and the transmitted beam was used to excite SEW. A copper film (≈ 1 μm thick) was deposited by evaporation on a clean glass microscope slide in a vacuum ($\sim 10^{-6}$ Torr) after argon–ion sputtering. Oxygen-free, high conductivity copper was used for deposition. Two right-angle BaF_2 prisms were placed on the copper film. The optimum gap height between the prism and the metal surface was found to be 25 μm. This gap height was maintained by Mylar spacers and a spring clamp holding the prism against the spacers.

The angle of incidence θ inside the prism, was found to vary from 45.0° at 1080 cm^{-1} to 46.0° at 925 cm^{-1} for optimum coupling and decoupling. These angles coincided with the critical angle values for BaF_2 at the respective frequencies. The optimum coupling of SEW is sensitive to even a 0.1° change in the angle, so a fine goniometer (0.1°) was used for this purpose.

For propagation distance measurements, the second prism was moved from 0.7 to 3.0 cm in steps of 0.2

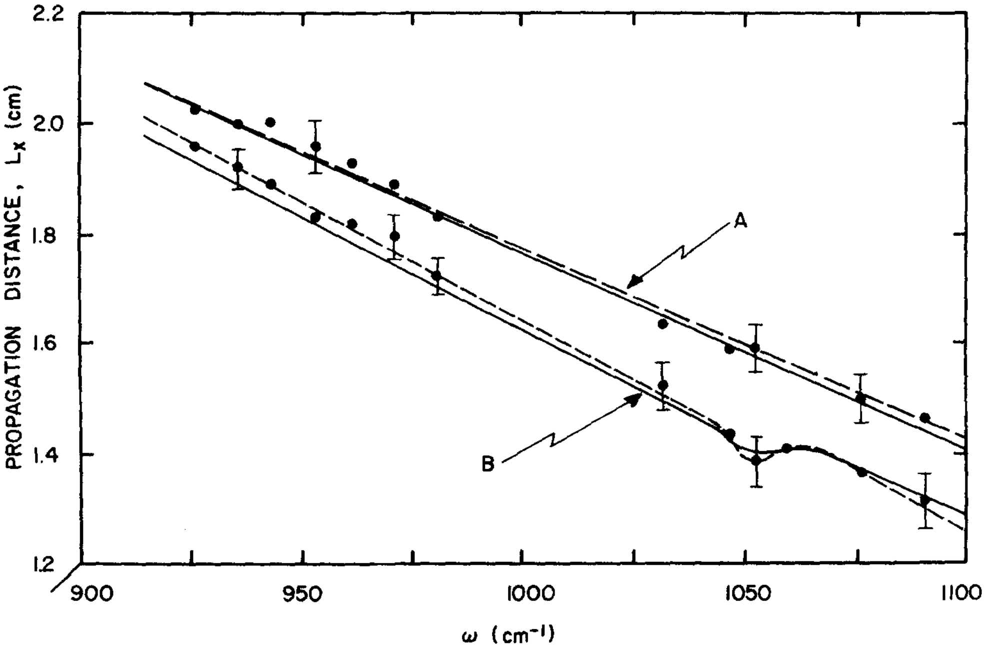

FIG. 3. Dashed lines are experimental values of the propagation distance L_{0x} for Cu (curve A) and L_x for Cu with 15 Å thick cellulose acetate (curve B). Solid curves are corresponding theoretical fits.

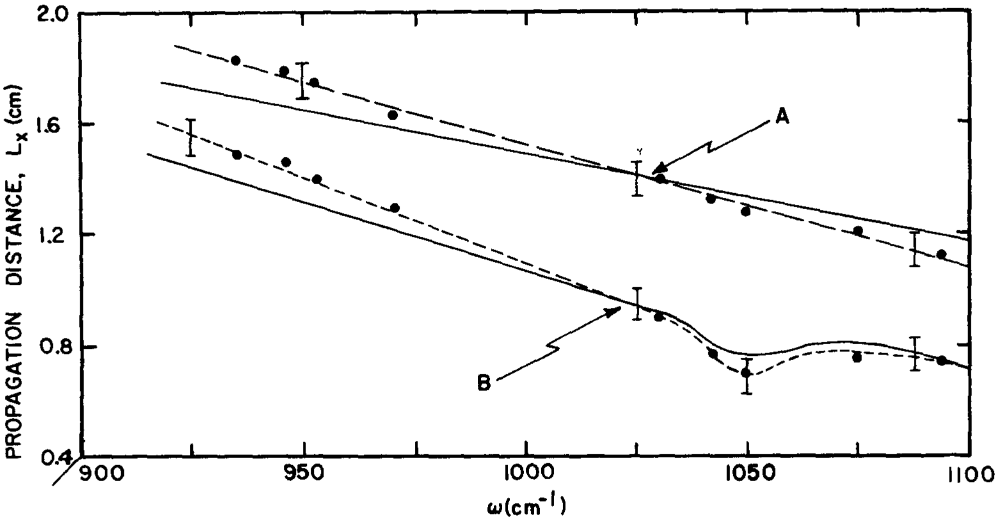

FIG. 4. Dashed lines are experimental values of the propagation distance L_{0x} for Cu (curve A) and L_x for Cu with 75 Å thick cellulose acetate (curve B). Solid curves are corresponding theoretical fits.

cm using a fine micrometer attached to the prism. The details of the mechanism used are described elsewhere.[8] At each step, the relative intensity $I(\omega, x)$ for the separation distance between the prisms was recorded. From the slope of a semilogarithmic plot of $I(\omega, x)$ vs x, L_{0x} was determined for the Cu film. $L_{0x}(\omega)$ vs wavenumber ω is plotted in Fig. 3 for film 1 and is represented by the dashed line A. The same is plotted in Fig. 4 for film 2. The two Cu films were deposited at different times.

After measuring L_{0x}, the Cu films were dipped for 5 sec in a solution of cellulose acetate dissolved in acetone, producing a layer of acetate after the acetone evaporated. The thickness of the cellulose acetate on the Cu was estimated by ellipsometry.[10,11] The computer program by McCrackin *et al.*,[12] was used to determine thickness from the ellipsometric data. Thicknesses of 15 ± 10 Å for film 1 and 75 ± 15 Å for film 2 were obtained.

The same procedure was used to measure $L_x(\omega)$ for the Cu–cellulose acetate–air system as was used for L_{0x}. The results are plotted in Fig. 3 for film 1 and in Fig. 4 for film 2, and are represented by the dashed lines labeled B. By extrapolating the observed signal to zero prism separation, it was found that the coupling efficiency of SEW to the copper film was not changed by the addition of the cellulose acetate layer.

Substituting the values of $L_{0x}(\omega)$ and $L_x(\omega)$ of film 1 in Eq. (5), and plotting $T(\omega, x)$ vs ω for $x = 3.0$ cm, yield the SEW transmission spectra for the 15 Å cellulose acetate film on Cu shown in Fig. 5.

In order to compare our results with theory, the optical constants for cellulose acetate were needed. Infrared transmission spectra of cellulose acetate films of various thicknesses were measured to obtain the absorption coefficient α in a frequency range from 900 to 1200 cm⁻¹. This is plotted in Fig. 6. The refractive index of $n = 1.4$ was also estimated from the

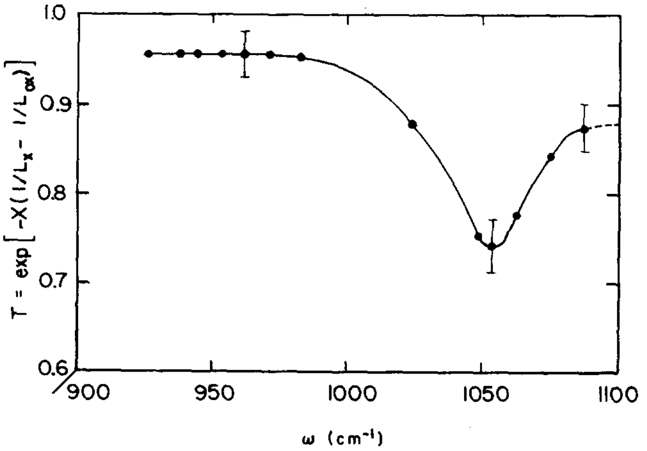

FIG. 5. Transmission $T(\omega, x)$ for a 15 Å thick cellulose acetate film on Cu with $x = 3$ cm.

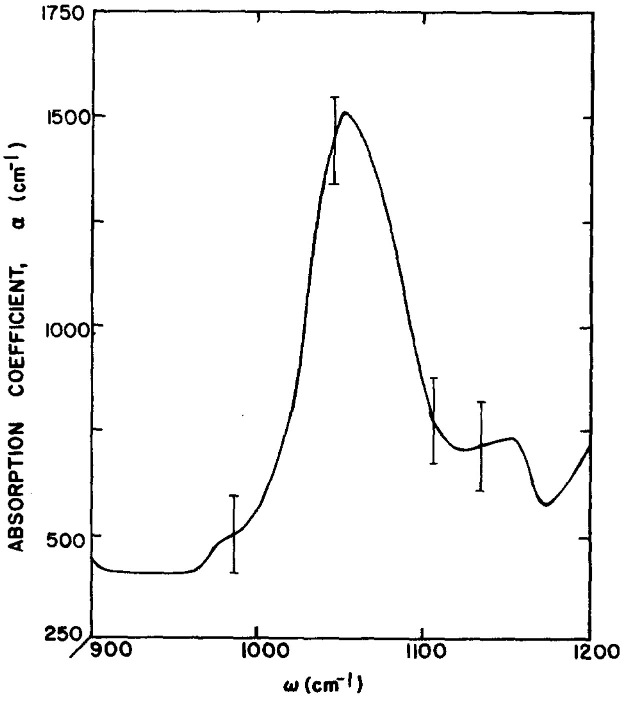

FIG. 6. Absorption coefficient α vs wavenumber ω for cellulose acetate.

reflectivity. From α and n, we calculated the dielectric constants for cellulose acetate.

B. Cellulose acetate films

Since the dielectric constant of thin copper films varies from film to film, L_{0x} was measured for each film. Substituting the measured values of L_{0x} in Eq. (1), we obtained the ratio ω_p^2/ω_τ. For bulk Cu, $\omega_p = 6.5\times 10^4$ cm^{-1} and $\omega_\tau = 266$ cm^{-1} were obtained[1] from a Drude model fit of available data.[13] It has been observed that ω_τ may vary as much as 20% for thin metal films while the variation in ω_p is small.[8,14] By fixing ω_p near 6.5×10^4 cm^{-1}, the corresponding values of ω_τ for the Cu films were obtained from the ratio ω_p^2/ω_τ.

For film 1, the calculated values of L_{0x} from Eq. (1) are plotted in Fig. 3, represented by solid line A. Using $\omega_p = 6.5\times 10^4$ cm^{-1} and $\omega_\tau = 385$ cm^{-1}, the calculated values of L_{0x} from Eq. (1) lie on the experimental curve. Furthermore, Δ_2 as given in Eq. (4), was calculated for the 25 Å cellulose acetate film on Cu. Using these calculated values of L_{0x} and Δ_2 in Eq. (3), L_x was obtained and plotted in Fig. 3 (dashed curve B). Using $\omega_p = 6.0\times 10^4$ cm^{-1}, $\omega_\tau = 390$ cm^{-1}, and $d = 150$ Å to obtain L_x for film 2, the same procedure was followed, but the experimental values of L_{0x} are used instead of the theoretical values of L_{0x} to obtain L_x. The results are plotted in Fig. 4.

Our experimental values of L_{0x} for different Cu films lie within 20% of the calculated values of L_{0x} obtained[1] from the bulk dielectric constants of Cu.[13]

In comparing our experimental values of L_x with theory, 25 and 150 Å film thicknesses were used for cellulose acetate films 1 and 2, respectively. These values of thickness are higher than those obtained by ellipsometry. It has been observed before that ellipsometry measures thicknesses to be less than other techniques.[15] This discrepancy could be due to the fact that in our technique, the results are integrated over a large distance on Cu, whereas in ellipsometry, the beam is incident on a small area. Therefore, the thickness values obtained from SEW measurements are the mean thicknesses of the cellulose acetate film on copper.

For the nonresonance part of the SEW spectra of the absorbing film (that is, when $\epsilon_2'' \simeq 0$), it can be easily shown from Eqs. (3) and (5) that

$$d = \frac{\omega_p^2}{4\pi^2\omega_\tau\omega^2 x}\left(\frac{\epsilon_2'}{\epsilon_2'-1}\right)\ln\left(\frac{I_0}{I}\right). \tag{7}$$

This equation shows that the mean thickness of the overlayer material on copper can be estimated if the real part of the dielectric constant ϵ_2' and the percent transmission at a nonresonance frequency for the overlayer material are known.

C. Physisorbed benzene

For physisorption experiments, a vacuum chamber with $\mathrm{BaF_2}$ windows for incoming and outgoing infrared beams was mounted on a goniometer accurate to 0.014°. A small brass Dewar was placed below the Cu slide and a Chromel–Alumel thermocouple was attached to the Cu slide. The distance between the Dewar and the windows was kept large enough to avoid condensation on the windows. Two $\mathrm{BaF_2}$ prisms ($x = 3.0$ cm) were clamped down to a Cu film on 25 μm thick Mylar spacers to maintain an optimum gap height. By rotating the entire chamber with the goniometer, the angle of incidence of the incoming beam was adjusted to excite SEW on the Cu film.

On top of the vacuum chamber, a sealed stainless steel tube of benzene was connected through a valve. The chromatographic grade, thiophene-free benzene was frozen by submerging the tube in liquid $\mathrm{N_2}$ before opening the valve to evacuate the tube. A vacuum of the order of 10^{-4} Torr was achieved, and the Cu slide was cooled to 190 °K. The SEW intensity $I_0(\omega, x)$ was then recorded.

The liquid $\mathrm{N_2}$ Dewar was then moved away from the tube containing the frozen benzene, and the benzene was allowed to vaporize. When an observable decrease in SEW intensity was measured, enough benzene had been condensed on the Cu slide and the valve to the tube containing the benzene was closed. After the system had stabilized, the intensity $I(\omega, x)$ was measured.

The SEW transmission T was obtained by the ratio I/I_0. In Fig. 7, the percent transmission $T(\omega, x)$ is plotted vs ω for three different thicknesses of benzene on copper. A similar procedure was used to study physisorbed distilled water on copper. The percent transmission $T(\omega, x)$ for water is plotted vs ω in Fig. 8.

From the refractive index values obtained by Anderson and Person[16] for the 975 cm^{-1} resonance of crystal benzene and the experimental values of I_0/I from Fig. 7, an estimate of thicknesses for physisorbed benzene on Cu was made using Eq. (7). For spectra A, B, and C in Fig. 7, the thicknesses of benzene were estimated to be 25, 10, and 5 Å, respectively. In the same way, using $\epsilon_2 \approx 1.49$[17] for water, a thickness of 20 Å was estimated for Fig. 8.

Finally, a computer program for Eq. (6) was used to calculate theoretical curves for the SEW spectra in Figs. 7 and 8.

IV. DISCUSSION

An infrared spectrum of solid benzene measured by Zwerdling *et al.*,[18] is given in Fig. 9 for comparison with the SEW spectra of physisorbed benzene on copper in Fig. 7. No observable shift was found in the 1037 or the 975 cm^{-1} resonances of physisorbed benzene in the SEW spectra compared to the infrared spectrum of solid benzene. The observation of the 975 cm^{-1} resonance of physisorbed benzene in the SEW spectra shows that physisorbed benzene exists in asymmetric environment since that resonance is not observed in the gas phase. The absorption intensity ratio of the 975 cm^{-1} resonance to the 1037 cm^{-1} resonance of physisorbed benzene in Fig. 7 is higher than that of solid benzene in Fig. 9. The 975 cm^{-1} resonance of the benzene is a C–H out-of-plane vibration and the 1037 cm^{-1} resonance

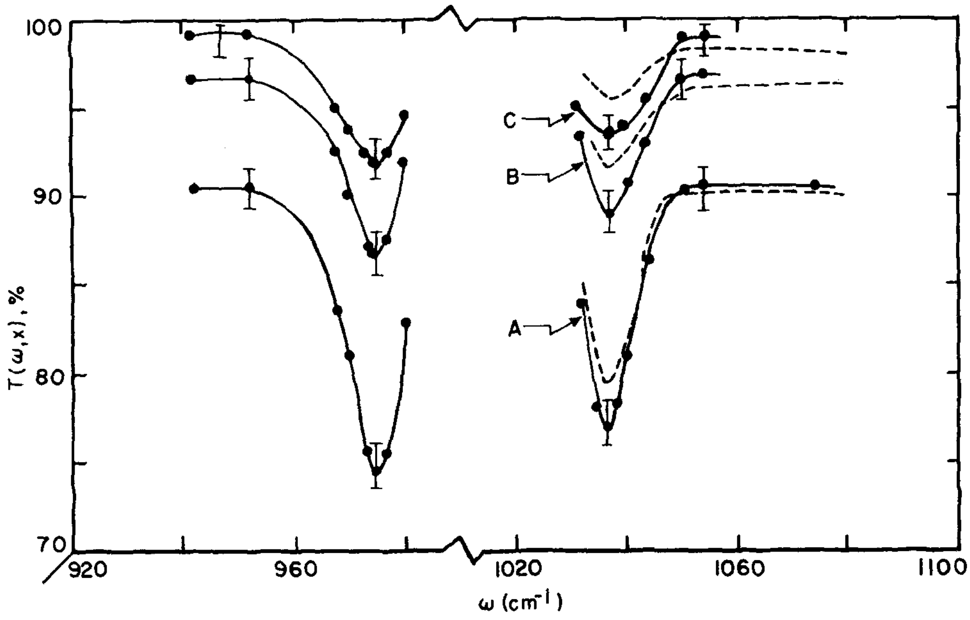

FIG. 7. Percent transmission $T(\omega, x)$ for physisorbed benzene on Cu. Solid lines are experimental values and dashed lines are calculated for 25 Å in curve A, 10 Å in B, and 5 Å in C. Note discontinuity in the wavenumber scale.

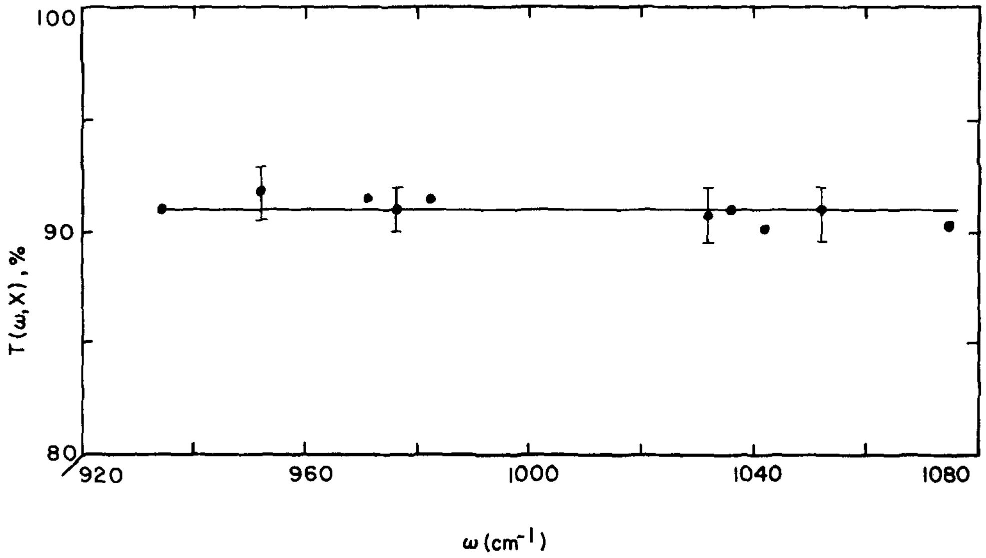

FIG. 8. Percent transmission $T(\omega, x)$ for physisorbed water on Cu. Dots represent experimental data and the solid line is calculated for 20 Å thick physisorbed water.

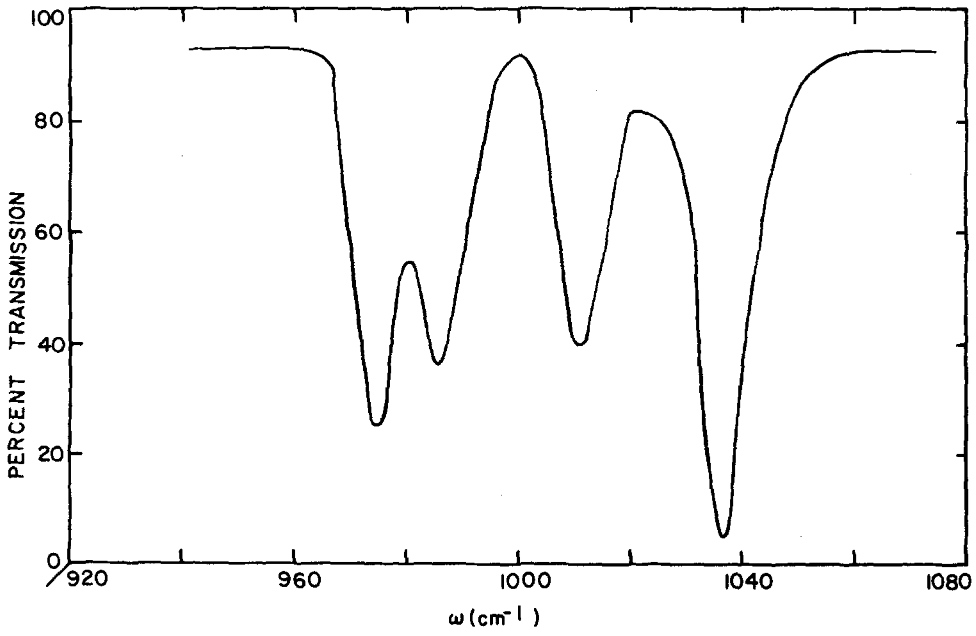

FIG. 9. Infrared transmission spectrum for solid benzene.

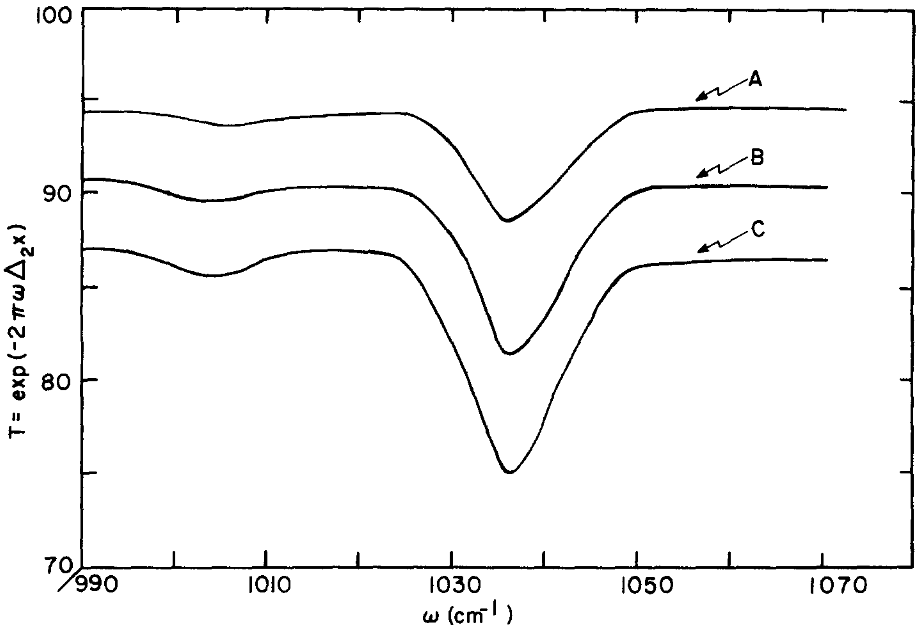

FIG. 10. Calculated SEW spectra of solid benzene on Cu for 15 Å in curve A, 25 Å in B, and 35 Å in C.

is a C–H in-plane bending vibration.[19] The theoretical calculations have shown that the magnitude of the z component is very large compared to the x component of the SEW electric field.[1] If benzene molecules lie flat on a perfectly plane copper surface, the in-plane bending vibration should not be observed; but the observation of the 1037 cm^{-1} resonance indicates that benzene is randomly oriented with respect to the copper surface or the surface roughness on an atomic scale is important. Note that broadening of both resonances is observed for a 5 Å thick physisorbed benzene in Fig. 7.

The SEW spectra in Fig. 7 also show a high degree of sensitivity at nonresonance frequencies to thickness changes in the overlayer material. The ordinary infrared spectrum is only sensitive very close to resonance frequencies. This nonresonant sensitivity of SEW spectra has allowed us to estimate the mean thickness of physisorbed benzene on copper down to 5 Å.

In order to determine the accuracy of the thickness measurements, an error analysis for Eq. (6) was carried out. Our calculations show that a 10% error in ω_p or a 20% error in ω_τ will shift the percent transmission T at all frequencies in an SEW spectrum by 2%. A 10% change in the refractive index n of solid 25 Å thick benzene on copper will shift T by 2% also. A 10% change in the extinction coefficient k of solid benzene does not shift T at nonresonance frequencies but rather at near-resonance frequencies and by approximately 2%. For comparison, the SEW spectra of 15, 25, and 35 Å thick benzene on copper is given in Fig. 10. This demonstrates that the SEW theory can be used to predict the mean thicknesses of adsorbed molecules on metal sur-

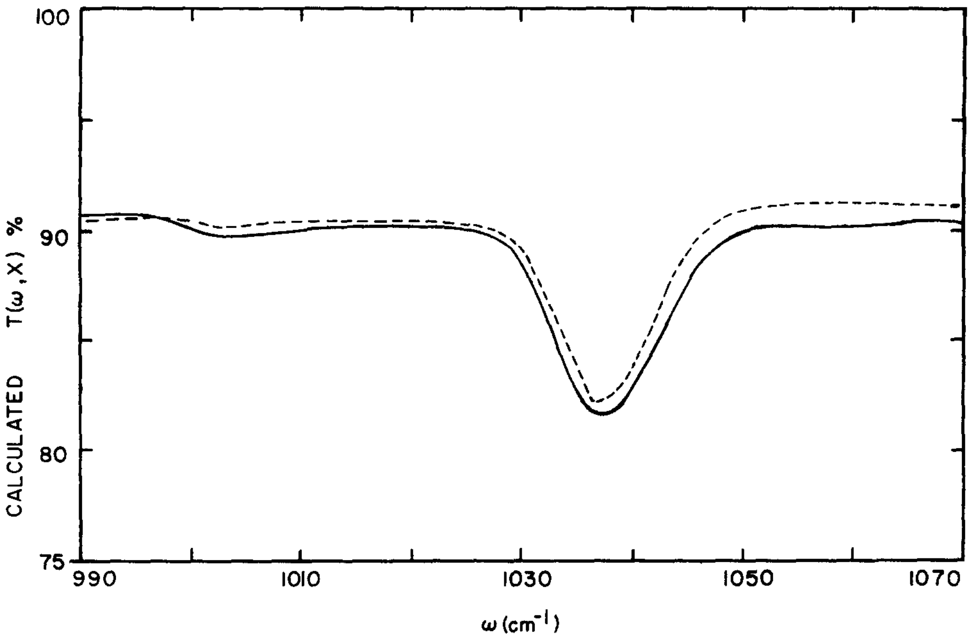

FIG. 11. Calculated SEW spectra for Cu–Cu$_2$O–C$_6$H$_6$–air system (dashed curve) with d = 20 Å for Cu$_2$O and d = 25 Å for C$_6$H$_6$, and for Cu–C$_6$H$_6$–air system (solid curve) with d = 25 Å for C$_6$H$_6$.

faces if all the other parameters for the given system are well known.

The Cu films used in these experiments were exposed to air upon their removal from the evaporation chamber. This causes about a 20 Å thick Cu_2O layer to form on the Cu film.[20] To determine if the SEW spectra were affected by Cu_2O layers on the Cu substrate, a $Cu-Cu_2O-C_6H_6$-air system was assumed in which $d = 20$ Å for the Cu_2O layers and $d = 25$ Å for the benzene. The dielectric constants for Cu_2O were obtained from Ref. 21. For this system, $L_x(\omega)$ was calculated from a computer program for four media. This program is based on the equation for the multimedia dispersion relation[22] simplified to save computer time in a manner analogous to the delta method used for three media.[1] The approximation requires that both overlayers be thin. Next, the thickness of the benzene was set equal to zero and $L_{0x}(\omega)$ was obtained. Substituting the calculated values of L_{0x} and L_x in Eq. (5), $T(\omega, x)$ was determined for the assumed four-layer system, plotted in Fig. 11. It is plotted along with the calculated $T(\omega, x)$ for a $Cu-C_6H_6$-air system in which $d = 25$ Å for benzene. The difference of about 1% between the two curves is within the experimental error.

By using macroscopic values of dielectric constants of solid benzene[16] in the SEW theory, the theoretical SEW spectra for the 1037 cm^{-1} resonance of physisorbed benzene in Fig. 7 compares favorably to that of the experimental. It is suggested that the differences at frequencies near resonance might be due to changes in the dielectric constants of the thin layers of physisorbed benzene on a copper surface. This may also account for the broadening of the absorption lines in the thinnest film.

V. CONCLUSIONS

It has been demonstrated that surface electromagnetic wave spectroscopy can be used to measure resonance and nonresonance absorption due to adsorbed molecules and very thin films on metal surfaces in the infrared. The experimental results compare quite well with the previously developed continuum theory used to predict absorption of SEW due to thin films.[1] It has been shown that the theory can be used in conjunction with the experimental results to estimate the mean thicknesses of very thin overlayer materials on metal surfaces.

This SEW technique can be successfully used to study adsorbed molecules, such as benzene; oxides, such as Cu_2O on copper; thin polymer films, such as cellulose acetate films; and probably adhesives on metal surfaces. Especially in the far infrared where SEW can propagate very long distances on metal surfaces, surface electromagnetic wave spectroscopy can be used to obtain vibrational and hindered rotational spectra of adsorbed molecules on metal surfaces. With tunable infrared lasers, these studies will be extended into other ranges of the infrared.[23,24]

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[1] R. J. Bell, R. W. Alexander, Jr., C. A. Ward, and I. L. Tyler, Surf. Sci. **48**, 253 (1975).

[2] A. Otto, in *Festkorperprobleme XIV*, edited by H. J. Queisser (Vieweg, Braunschweig, 1974).

[3] R. H. Ritchie, Surf. Sci. **34**, 1 (1973).

[4] K. L. Kliewer and R. Fuchs, *Advances in Chemical Physics*, edited by I. Prigogine and S. A. Rice (Wiley, New York, 1974), Vol. 27, p. 355.

[5] E. Burstein, W. P. Chen, Y. J. Chen, and A. Hartstein, J. Vac. Sci. Technol. **11**, 1004 (1974).

[6] J. Schoenwald, E. Burstein, and J. M. Elson, Solid State Commun. **12**, 185 (1973).

[7] J. D. McMullen, Solid State Commun. **17**, 331 (1975).

[8] D. Bryan, D. L. Begley, K. Bhasin, R. W. Alexander, R. J. Bell, and R. Gerson, Surf. Sci. (to be published).

[9] R. J. Bell, R. W. Alexander, Jr., W. F. Parks, and G. Kovener, Opt. Commun. **8**, 147 (1973).

[10] K. H. Zaininger and A. G. Revesz, RCA Rev. **25**, 85 (1964).

[11] F. L. McCrackin, C. Passaglio, R. R. Stromberg, and H. Steinberg, J. Res. Natl. Bur. Stand. Sect. A **67**, 363 (1963).

[12] F. L. McCrackin and J. P. Colson, Natl. Bur. Stand. (U.S.) Tech. Note **242** (1964).

[13] A. P. Lenham and D. M. Treherne, J. Opt. Soc. Am. **56**, 683 (1966); L. G. Schulz, *ibid.* **44**, 357 (1954).

[14] P. Halevi, in *Proceedings on the Third International Conference on Thin Films, Budapest, August*, 1975 (Elsevier Sequoia, S. A., Lausanne, to be published).

[15] Y. S. Lipatov and L. M. Sergeeva, *Adsorption of Polymers* (Wiley, New York, 1974).

[16] G. R. Anderson and W. B. Person, J. Chem. Phys. **36**, 62 (1962).

[17] A. N. Rusk, D. Williams, and M. R. Querry, J. Opt. Soc. Am. **61**, 895 (1971).

[18] S. Zwerdling and R. S. Halford, J. Chem. Phys. **23**, 2221 (1955).

[19] G. Varsanyi, *Assignments for Vibrational Spectra of Seven Hundred Benzene Derivatives* (Wiley, New York, 1974).

[20] T. N. Rhodin, J. Am. Chem. Soc. **73**, 3143 (1951).

[21] P. Dawson, M. H. Hargreave, and G. R. Wilkinson, J. Phys. Chem. Solids **34**, 2201 (1973).

[22] C. A. Ward, K. Bhasin, R. J. Bell, R. W. Alexander, and I. L. Tyler, J. Chem. Phys. **62**, 1674 and 4960 (1975).

[23] P. P. Sorokin, J. J. Wynne, and J. R. Lankard, Appl. Phys. Lett. **22**, 342 (1973).

[24] I. L. Tyler, R. W. Alexander, and R. J. Bell, Appl. Phys. Lett. **27**, 346 (1975).