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RESONANT EXCITATION OF PLASMONS IN THIN FILMS BY ELECTROMAGNETIC WAVES*

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The resonant excitation in thin films of bulk plasma waves by incident electromagnetic waves is studied, and is shown to lead to structure in the reflectance, transmittance, and absorptance.

Anomalous absorption of obliquely incident p-polarized radiation at the plasma frequency of a silver film was first observed by McAlister and Stern.[1] The effect, first predicted by Ferrell and Stern,[2] was explained as the excitation of surface plasma oscillations.[3] This Letter shows that bulk plasma waves can also be excited by incident electromagnetic waves and under certain conditions their resonant coupling may be observed in the transmittance (T), reflectance (R), or absorptance (A) spectra of thin metallic (or semiconductor) films. These resonances are related to the Tonks-Dattner resonances,[4] and occur when

$$(\lambda_L)_n = 2d/n, \quad n = 1, 3, 5, \cdots, \tag{1}$$

where $(\lambda_L)_n$ is the normal component of the bulk longitudinal plasma wavelength and d is the film thickness.

Consider a plasma slab of thickness d surrounded by vacuum on both sides. Since only radiation with an electric field component normal to the plasma surface will excite plasma waves, we consider only p-polarized, plane electromagnetic waves incident at an angle θ. If we assume that only transverse waves ($\vec{k}_T \cdot \vec{E}_T = 0$) exist in the plasma and neglect longitudinal or irrotational waves ($\vec{k}_L \times \vec{E}_L = 0$), we obtain the usual Fresnel equations for T and R:

$$T^F = \left| \frac{4\alpha\beta \exp(i\psi_T)}{(\alpha+\beta)^2 - (\alpha-\beta)^2 \exp(i2\psi_T)} \right|^2,$$

$$R^F = \left| \frac{(\alpha^2-\beta^2)[1-\exp(i2\psi_T)]}{(\alpha+\beta)^2 - (\alpha-\beta)^2 \exp(i2\psi_T)} \right|^2, \tag{2}$$

where

$$\alpha = \epsilon_T \cos\theta,$$

$$\beta = (\epsilon_T - \sin^2\theta)^{1/2},$$

$$\psi_T = \vec{n} \cdot \vec{k}_T d = \beta(d\omega/c) = \beta(2\pi d/\lambda).$$

Here ϵ_T is the transverse dielectric of the plasma, i.e., $\epsilon_T = (c/\omega)^2 \vec{k}_T \cdot \vec{k}_T$; ω is the frequency of the incident radiation; c the vacuum speed of light; and β is the normal component of $\vec{k}_T$ in units of the vacuum wave vector ω/c. Because they excluded bulk longitudinal plasma waves, McAlister and Stern[1] used Eqs. (2) in their theory.

But if we include both transverse and longitudinal waves in the plasma, the equations for T and R become[5]

$$T = \left| \frac{4\alpha\{\gamma[1-\exp(i2\psi_T)]\exp(i\psi_L) + \beta[1-\exp(i2\psi_L)]\exp(i\psi_T)\}}{\Delta} \right|^2,$$

$$R = \left| \frac{[1-\exp(i\psi_T)\exp(i\psi_L)]^2 AD - [\exp(i\psi_T) - \exp(i\psi_L)]^2 BC}{\Delta} \right|^2, \tag{3}$$

where

$$A=\alpha-\beta-\gamma,\quad B=\alpha-\beta+\gamma,\quad C=\alpha+\beta-\gamma,\quad D=\alpha+\beta+\gamma,$$

$$\Delta=[1-\exp(i\psi_T)\exp(i\psi_L)][D^2-A^2\exp(i\psi_T)\exp(i\psi_L)]-[\exp(i\psi_T)-\exp(i\psi_L)][B^2\exp(i\psi_T)-C^2\exp(i\psi_L)]$$

$$\psi_L=\vec{n}\cdot\vec{k}_L d=\left(\frac{ck_L}{\omega}\right)_n\left(\frac{2\pi d}{\lambda}\right),$$

and

$$\gamma=\sin^2\theta[1-\epsilon_T](ck_L/\omega)_n^{-1}.$$

$(ck_L/\omega)_n$ is the normal-component wave vector (in units of ω/c) of the longitudinal wave, whose dispersion relation $k_L(\omega)$ is given by $\epsilon_L(k_L,\omega)=0$, ϵ_L being the longitudinal dielectric. Thus T and R are easily determined if the dispersion relation of both waves is given. Note that expressions (3) reduce to (2) when $\gamma, \exp(i\psi_L)\to 0$.

To see the qualitative behavior of Eqs. (3) we approximate the dispersion relations by

$$(ck_T/\omega)^2=\epsilon_T\simeq 1-(\omega_p/\omega)^2,$$

$$\left(\frac{ck_L}{\omega}\right)^2\simeq\frac{5}{3}\left(\frac{c}{v_F}\right)^2\left[\left(\frac{\omega}{\omega_p}\right)^2-1\right],\qquad(4)$$

where v_F is the Fermi velocity of the electrons in the metallic plasma. From Eqs. (4) we see that $\lambda_L\ll\lambda_T$, $\lambda<\lambda_T$; so for $d<\lambda_p$, where λ_p is the vacuum wavelength at the plasma frequency ($\lambda_p=2\pi c/\omega_p$), we can make the approximation $\exp(i\psi_T)\simeq 1$ and Eqs. (3) become

$$T\simeq\frac{\alpha^2(1+\cos\psi_L)}{\alpha^2(1+\cos\psi_L)+\gamma^2(1-\cos\psi_L)},$$

$$R\simeq\frac{\gamma^2(1-\cos\psi_L)}{\alpha^2(1+\cos\psi_L)+\gamma^2(1-\cos\psi_L)}.\qquad(5)$$

In obtaining (5) we have assumed α and γ to be real; i.e., we have assumed undamped waves.

Since $\gamma<\alpha$ except when $\omega\simeq\omega_p$, Eqs. (5) show that most of the energy is transmitted except when $\cos\psi_L=-1$, or when the condition given by Eq. (1) is satisfied. In other words, the reflectance (transmittance) has a relative maximum (minimum) whenever the slab thickness is equal to an odd number of half wavelengths of the longitudinal wave. Near ω_p, where $\gamma\gtrsim\alpha$ a broader maximum (minimum), corresponding to a surface wave, is superimposed on these resonance maxima (minima). At frequencies so close to ω_p that $\lambda_L>d$ we may approximate $\exp(i\psi_L)$ by $1+i\psi_L$ and Eqs. (3) reduce to

$$T=\left|\frac{2\alpha}{2\alpha-i\gamma\psi_L}\right|^2=\left|\frac{2\epsilon_T}{2\epsilon_T-i(2\pi d/\lambda)(\sin^2\theta/\cos\theta)(1-\epsilon_T)}\right|^2,$$

$$R=\left|\frac{i\gamma\psi_L}{2\alpha-i\gamma\psi_L}\right|^2=\left|\frac{i(2\pi d/\lambda)(\sin^2\theta/\cos\theta)(1-\epsilon_T)}{2\epsilon_T-i(2\pi d/\lambda)(\sin^2\theta/\cos\theta)(1-\epsilon_T)}\right|^2.\qquad(6)$$

It is interesting to note that Eqs. (6) are almost identical to the corresponding expressions in the McAlister and Stern paper,[6] despite the fact that their expressions came from the approximation $\exp(i\psi_T)\simeq 1+i\psi_T$ because $\lambda_T>d$; while in our expressions we neglected the effect of the transverse wave [$\lambda_T\gg d$ so $\exp(i\psi_T)=1$] and considered the effect of long-wavelength ($\lambda_T>d$) longitudinal plasma waves.

We have numerically computed both the Fresnel expressions (2) and Eqs. (3) for T and R using dispersion relations numerically solved from the standard expressions[7] for the dielectric components of a plasma,

$$\epsilon_T=1-\frac{\omega_p^2}{\omega(\omega+i/\tau)}\frac{3}{2a^2}\left[\frac{1+a^2}{a}\tan^{-1}a-1\right],$$

$$\epsilon_L=1-\frac{[\omega_p^2/\omega(\omega+i/\tau)](3/a^2)[1-a^{-1}\tan^{-1}a]}{1+i/\omega\tau[1-a^{-1}\tan^{-1}a]},\qquad(7)$$

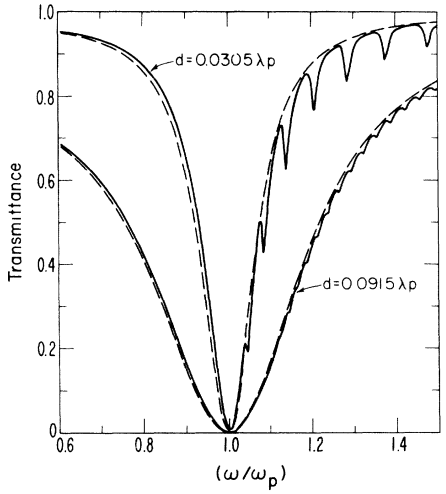

FIG. 1. Transmittance as a function of frequency for plasma slabs of two thicknesses. The dashed curves correspond to the usual Fresnel equations (2) and the solid curves correspond to the more general equations (3). These results are calculated for p-polarized radiation incident at an angle of 60° on an electron plasma slab with a Fermi velocity of 1.4×10^8 cm/sec and a collision time corresponding to $\omega_p\tau = 100$.

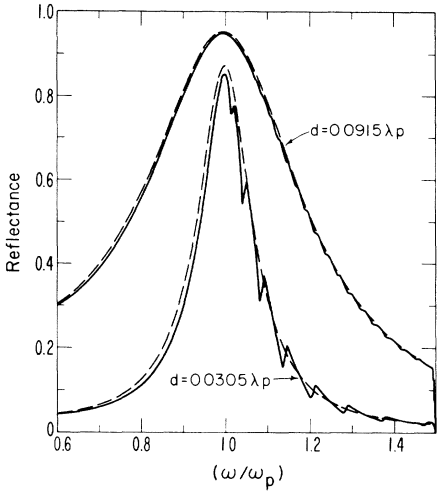

FIG. 2. Reflectance as a function of frequency for plasma slabs of two thicknesses. The dashed and solid curves have their significance and all parameters and conditions defined precisely as in Fig. 1.

where

$$a^2 = \frac{-v_F{}^2\vec{k}\cdot\vec{k}}{(\omega + i/\tau)^2},$$

and τ is the collision time. The numerical parameters used in the calculation were $v_F = 1.4\times10^8$ cm/sec, $c = 3\times10^{10}$ cm/sec, and $\omega_p\tau = 100$. The results for 60° incidence are shown in Figs. 1-3 for thicknesses $d = 0.0305\lambda_p$ and $0.0915\lambda_p$. For silver, with a plasma wavelength $\lambda_p = 3275$ Å and a Fermi velocity $v_F = 1.4\times10^8$ cm/sec, these thicknesses correspond to 100 and 300 Å.

While such thicknesses and resolutions ($\Delta\lambda/\lambda \sim 10^3$) are attainable, there is one difficulty which may present possible limitations on experimental observations of the resonances. The expressions for the dielectric functions (7) are calculated for a plasma of infinite extent with some constant collision frequency $1/\tau$. But to warrant neglect of surface scattering the mean free path of the electrons, $\lambda_m = v_F\tau$, must be less than the thickness, so our condition on the thickness becomes $\lambda_m < d < \lambda_p$ or

$$\omega_p\tau\lambda_D < d < \lambda_p. \tag{8}$$

Since the screening length, $\lambda_D \sim (v_F/\omega_p)$, for silver is about 2.4 Å, this condition may be somewhat difficult to satisfy with complete adequacy for $\omega_p\tau = 100$ unless the film thickness is carefully chosen. Thus if scattering at the surface appreciably alters the bulk properties of the plasma these resonances may be difficult to observe in metallic plasmas. But in that case the experiment may still be possible with semiconductor plasmas which have smaller thermal or Fermi velocities. In fact the plasmon resonance and dispersion in silver and other noble metals may differ markedly from that predicted by our free-electron calculation because of the interaction with core electrons (hybrid resonance). In silver the actual dispersion relation for plasmons may

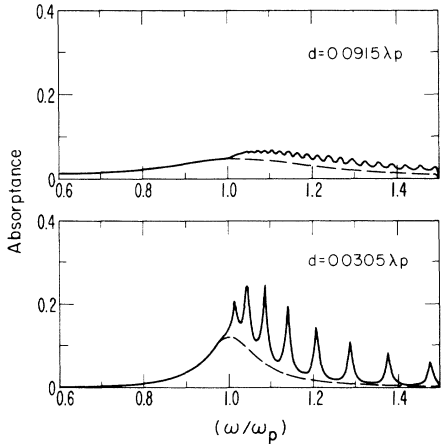

FIG. 3. Absorptance as a function of frequency for plasma slabs of two thicknesses. The dashed and solid curves have their significance and all parameters and conditions defined precisely as in Fig. 1.

correspond to a weaker dependence of plasma frequency on wave number than that given here; such real metal effects could modify our conclusions concerning the resonant peaks, but we have adopted a free-electron model because of its analytical simplicity and utility as an example.

In conclusion we wish to point out that Eqs. (3) are quite general and apply to any system possessing longitudinal electric polarization waves which are noninteracting with the transverse electromagnetic waves. Thus, for example, they may be applied to a polar crystal such as an alkali halide which possesses a longitudinal optic mode.

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ANGULAR-CORRELATION FUNCTIONS OF DIATOMIC ROTATORS IN ALKALI HALIDES

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For the first time, angular-correlation functions of diatomic rotators in solids have been determined experimentally using vibration-rotation spectra. As samples we used OH^- and OD^- in KCl. Maxima and minima of the correlation function show an isotopic shift.

Random rotation or tumbling of diatomic molecules in gases, liquids, or solids represents a stationary process.[1] In accordance with the theorem[2] of Wiener and Khintchin, the angular autocorrelation function can therefore be calculated as the Fourier transform of the normalized absorption observed in the rotation spectrum or the vibration-rotation spectrum. For the vibration-rotation spectrum, the angular autocorrelation function is given by

$$\int_0^\infty I(\omega)\cos\omega t d\omega \cong \langle \vec{u}(0)\vec{u}(t)\rangle \cos(\omega_0 t) = 3\langle \cos\theta(0)\cos\theta(t)\rangle \cos\omega_0 t,$$

where $I(\omega)$ indicates the normalized absorption, ω_0 the frequency corresponding to the vibrational transition, and

$$\vec{u}(t) = [\sin\theta(t)\cos\varphi(t), \sin\theta(t)\sin\varphi(t), \cos\theta(t)]$$

the unit vector in the direction of the oscillating electric dipole. This equation has been derived by Gordon[3] and Brot[4] for liquids and gases. The correlation functions evaluated from our spectra of HCl and HBr in CCl_4 are in good agreement with those of CO in CCl_4, C_6H_{14}, etc., determined by Gordon[3] from spectra of Josien and Bulanin.[5]

The rotation or tumbling of OH^- and OD^- in alkali halides has been observed by dielectric relaxation,[6] and ultraviolet and infrared spectroscopy.[7] All measurements indicate a strong influence of a cubic crystal-field potential acting on the diatomic molecule as described by Devonshire[8] and Sauer.[9] Therefore we expected to find a special behavior of the angular-correlation functions of diatomic rotators in crystal fields. We have measured the vibration-rotation spectra on OH^- and OD^- in KCl near 3700 and 2700 cm^{-1} at room temperature. The corresponding autocorrelation functions, superposed by the vibrational decay function, are shown in Fig. 1. Group-theoretical considerations demonstrate the applicability of the above correlation functions for rotators in liquids and in local fields of cubic symmetry.[10] For short times ($t<0.5\times10^{-13}$ sec) the