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Polaritons in a spatially dispersive dielectric half space*

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An exact microscopic theory of volume and surface polaritons is developed for a spatially dispersive dielectric half space. No dielectric function is postulated; instead a collection of terms which is designated such arises naturally in the course of solving the microscopic equations that describe the response of the molecules to an external driving field. The excited states of the crystal are assumed to be Frenkel excitons which are treated in the tight-binding approximation. All intermolecular interactions are assumed to be of the point-dipole type. Formulas are derived for the reflection of *s*- and *p*-polarized light from the dielectric at arbitrary angle of incidence. Formulas are also given for the reflection of light inside a prism separated from the dielectric by a small gap as in attenuated-total-reflection experiments used to detect surface modes. Model calculations, using ZnSe parameters, exploring the effect of spatial dispersion on the optical properties are described.

I. INTRODUCTION

The purpose of this paper is to develop in a logical and consistent manner a microscopic theory of the optical properties of a semi-infinite molecular crystal. No assumptions concerning the dielectric function are made. Indeed, since the starting point is the set of Maxwell equations describing the interaction of point dipoles in vacuum with an electromagnetic field, there is no dielectric function for the material half space but it proves convenient in the course of solving the equations to identify a group of frequency-dependent terms that play the role of the dielectric function.

The effect of spatial dispersion on optical properties was first studied by Pekar[1] and later by Hopfield and Thomas.[2] These authors introduced the concept of the additional boundary condition (ABC) as a technique for solving the Maxwell equations when the material half space was treated as a continuous medium with a frequency- and wave-vector-dependent dielectric function.

Since Frenkel excitons approximate point excitations (electron and hole on the same molecule) they can exist in the surface planes. However, Wannier excitons being much greater in size, must distort completely in order for the center of gravity to penetrate the surface planes. This physical restriction from the surface region is analogous to that of the center of mass of a bubble between two parallel plates. The different ABC's postulated for Frenkel and Wannier excitons are one manifestation of their quite different physical properties.

In principle, the problem of guessing the appropriate ABC for a given type of exciton can be avoided if the nonlocal dielectric function $\epsilon(\omega, \vec{r}, \vec{r}')$ is known for all points $\vec{r}$ and $\vec{r}'$ inside the half space. For then Maxwell's equations can be solved and the optical properties of the solid calculated. Recently several groups[3-5] have adopted this approach and have claimed to have circumvented the specification of an ABC. The claims by these authors are premature to say the least since they approximated the function $\epsilon(\omega, \vec{r}, \vec{r}')$ by $\epsilon(\omega, \vec{r}-\vec{r}') \times \theta(z)\theta(z')$, where $\epsilon(\omega, \vec{r})$ is obtained by Fourier transformation of the bulk dielectric constant $\epsilon(\omega, \vec{K})$. The dangers in this approach are severe. In the case of Wannier excitons, it implies bulklike behavior right up to the surface. This is not correct since it has been shown that the nonlocal susceptibility for Wannier excitons should include terms depending on $|z+z'|$ arising from charge-image interactions near the boundary.[6]

Other more explicit criticisms have been advanced by Agranovich and Yudson,[7] who point out that the theory of Refs. 3 and 4 is only valid at one frequency ω which happens to fall outside the exciton band. Sipe and Van Kranendonk,[8] and Mead[9] have compiled other objections of a mathematical nature. In spite of the criticisms mentioned, the work of Refs. 3–5 contains some interesting discussions of polaritons in bounded media and offers physical insight into the effect of spatial dispersion on optical properties.

For Frenkel excitons microscopic theories have been derived[8-15] that require neither the use of an ABC nor an approximation for $\epsilon(\omega, \vec{r}, \vec{r}')$ near the surface of the crystal. The localization of the electron and hole on the same site reduces the problem of calculating the optical properties to that of finding the electromagnetic field of a discrete array of point dipoles. This approach has been largely ignored in Refs. 3–5 even though it has produced exact results which are useful as comparisons for approximate theories. The advantages of the microscopic approach are several. First, no ABC or dielectric function is assumed, the latter emerges naturally during the derivation; second, they are not restricted to systems where spatial dispersion is weak; third, they can be modified to account for surface reconstruction, adsorbed monolayers, and even dead layers.[16]

In this paper the microscopic theory is extended to include p-polarized excitations. The earlier work considered only the s-polarized optical properties and, consequently, could not describe the effect of spatial dispersion on surface polaritons which exist only as p-polarized excitations. Very recently reports of the observation of exciton surface polaritons in ZnO,[17] CuBr,[18] and anthracene[19] have been published. The latter involves a Frenkel exciton and the former, because of their small radii (≃20 Å), may be thought of as Frenkel-like.

This paper is organized as follows. We begin with a brief derivation of the reflection power of a half space, assuming a continuum model and the Pekar ABC $P=0$. Formulas are also derived for the reflection power of the attenuated-total-reflection (ATR) experiment used to detect surface polaritons. In Sec. III the problem is formulated for both s- and p-polarized fields. Then in Sec. IV the general solution of the p-polarized problem is outlined for the case of a driving field incident from vacuum on the semi-infinite crystal. Next, in Sec. V, the results of ordinary optics are recovered by assuming that spatial dispersion is absent. Section VI treats the case of an isotropic solid with spatial dispersion in detail since this is the simplest model problem. Section VII briefly considers other models, including the case of anisotropic molecules, and Sec. VIII comments briefly on surface polaritons and the theory of the ATR experiment. Section IX describes model calculations of the s- and p-polarized reflection power of the half space and the ATR p-polarized reflection powers showing the presence of surface polaritons.

II. CONTINUUM THEORY

An extremely useful way of checking the results of the microscopic theory in the limit of weak spatial dispersion is to calculate the reflectivity using the ABC $\vec{P}=0$ and the continuum model for the dielectric properties. In this section we find the reflection amplitudes for s and p polarization, first for the half space alone and then for the ATR configuration. In the latter case the light is reflected from the prism side of a glass vacuum interface parallel to the dielectric half space. The coordinate systems used in the calculations are shown in Fig. 1.

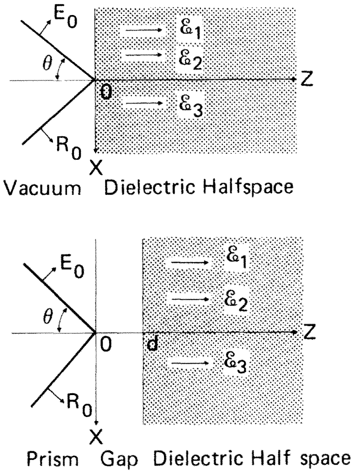

FIG. 1. Schematic representation of the right-handed coordinate system and the directions of the p-polarized incident and reflected electric field amplitudes for a dielectric half space without (top) and with a prism half space (bottom). For p polarization there are three fields $\mathcal{E}_i$ in the spatially dispersive medium.

The xz plane is taken to be the plane of incidence. All incident fields are assumed to be monochromatic with time dependence given by $e^{-i\omega t}$. The x dependence of the field amplitudes is taken to be $e^{i\kappa x}$, where κ is the projection of the wave vector onto the x axis. In the usual formulation the dielectric function of the half space is assumed to have the form

$$\epsilon(\omega, K) = \epsilon_0 + \frac{\omega_p^2}{\omega_T^2 + DK^2 - \omega^2 - i\omega\gamma}, \qquad (2.1a)$$

where ϵ_0 is the background dielectric constant; ω_T, the transverse exciton frequency; D, the spatial dispersion; γ, a phenomenological damping; K, the exciton wave vector; and ω_p^2, the "plasma frequency" containing the oscillator strength of the isolated transition as a factor.

A. Reflection from a dielectric half space

It is convenient to consider the reflection of p- and s-polarized incident fields separately. The formulas will be summarized only briefly since they are derivable from results available in the literature.

1. p polarization

For p polarization the continuity of E_x, H_y, and D_z across the interface plane $z=0$ yields equations sufficient to calculate the reflectivity in ordinary optics. However, in the presence of spatial dispersion the longitudinal mode mixes with the two transverse modes with the result that fields inside the dielectric have three components. For example, the electric field intensity inside the dielectric at the point $\vec{r} = (\vec{\rho}, z)$ is given by

$$E_\sigma(\vec{r}) = e^{i\vec{\kappa}\cdot\vec{\rho}} \sum_{j=1}^{3} \mathcal{E}_{j\sigma} e^{i\beta_j z}, \tag{2.1b}$$

where $\sigma = x, z$. Components of other vector fields are expressed in the same way. To solve the equations derived from the continuity relations an ABC is needed; we adopt the Pekar additional boundary condition that all the components of the polarization density $\vec{P}(\vec{r})$ are zero at the crystal surface. The results obtained in this way agree exactly with the microscopic theory in the limit of weak spatial dispersion.

The two transverse modes $j = 1, 2$ have total wave vectors $\vec{K}_j = (\vec{\kappa}, \beta_j)$ found by solving

$$c^2K^2/\omega^2 - \epsilon(\omega, \vec{K}) = 0\,. \tag{2.2}$$

Since the electric fields of these modes are perpendicular to their wave vectors, they satisfy

$$\kappa\mathcal{E}_{jx} + \beta_j\mathcal{E}_{jz} = 0, \quad j = 1, 2\,. \tag{2.3}$$

The longitudinal mode has total wave vector $\vec{K}_3 = (\vec{\kappa}, \beta_3)$, the magnitude of which satisfies

$$\epsilon(\omega, \vec{K}_3) = 0\,. \tag{2.4}$$

Since the electric field of this mode is parallel to its total wave vector, we have

$$\kappa\mathcal{E}_{3z} - \beta_3\mathcal{E}_{3x} = 0\,. \tag{2.5}$$

Propagation in the positive z direction in vacuum is described by the phase factor $e^{i\beta_0 z}$, where

$$\beta_0 = [(\omega/c)^2 - \kappa^2]^{1/2}\,. \tag{2.6}$$

Propagation in the same direction in the dielectric is described by $e^{i\beta_j z}$, where we may sometimes choose to write β_j in the form ($j = 1, 2$ only)

$$\beta_j = [n_j^2(\omega/c)^2 - \kappa^2]^{1/2}\,. \tag{2.7}$$

We shall sometimes refer to n_j as the refractive index of mode j when discussing the transverse modes, $j = 1, 2$.

The equations that must be solved for the reflection amplitude R_0 are

$$\beta_0(R_0 - E_0) = \frac{\omega}{c} \sum_{j=1}^{3} \mathcal{E}_{jx}, \tag{2.8}$$

$$\frac{\omega}{c}(R_0 + E_0) = -\sum_{j=1}^{3} (\beta_j\mathcal{E}_{jx} - \kappa\mathcal{E}_{jz}), \tag{2.9}$$

$$\sum_{j=1}^{3} \mathcal{P}_{j\sigma} = 0, \quad \sigma = x, z\,. \tag{2.10}$$

The last equation comes from the ABC applied to both components of the polarization density. By analogy with the relation $(\epsilon - 1)\vec{E} = 4\pi\vec{P}$, which holds for nondispersive materials, we assume that the amplitudes $\mathcal{P}_{j\sigma}$ and $\mathcal{E}_{j\sigma}$ are connected by

$$4\pi\mathcal{P}_{j\sigma} = (n_j^2 - 1)\mathcal{E}_{j\sigma}, \tag{2.11}$$

$$4\pi\mathcal{P}_{3\sigma} = -\mathcal{E}_{3\sigma}, \tag{2.12}$$

where $j = 1, 2$ in (2.11) and $\sigma = x, z$. Contrary to the conventional derivation we have here assumed that all the polarization $\vec{P}(\vec{r})$ comes from exciton transitions. This deviation is necessary in order to obtain a formula that agrees exactly with the one derived from the microscopic theory.

Straightforward manipulation of Eqs. (2.8)–(2.12) yields the following result for $r_p(\omega) = R_0/E_0$, the p-polarized reflection amplitude:

$$r_p(\omega) = -r_s(\omega) \times \left(\frac{n_1^2(\beta_0 + \beta_2)(\beta_2\beta_3 + \kappa^2) - n_2^2(\beta_0 + \beta_1)(\beta_1\beta_3 + \kappa^2)}{n_1^2(\beta_0 - \beta_2)(\beta_2\beta_3 + \kappa^2) - n_2^2(\beta_0 - \beta_1)(\beta_1\beta_3 + \kappa^2)}\right), \tag{2.13}$$

where $r_s(\omega)$ is the reflectivity for s-polarized fields given in Sec. II A2. We shall see that this result is also given by the microscopic theory in the limit of weak spatial dispersion, defined by $|a\beta_j| \ll 1$ for all $j = 1, 2, 3$.

2. s polarization

In s polarization there is no mixing of the longitudinal with the transverse modes. The electric incident and reflected field intensities are parallel to the y axis. Inside the crystal the electric field is the sum of two transverse components,

$$E_y(\vec{r}) = e^{i\vec{\kappa}\cdot\vec{\rho}} \sum_{j=1}^{2} \mathcal{E}_{jy} e^{i\beta_j z}\,. \tag{2.14}$$

Continuity of the tangential components of the electric and magnetic field intensities at the interface $z = 0$ yields

$$E_0 + R_0 = \mathcal{E}_{1y} + \mathcal{E}_{2y}, \tag{2.15}$$

$$\beta_0(E_0 - R_0) = \beta_1\mathcal{E}_{1y} + \beta_2\mathcal{E}_{2y}\,. \tag{2.16}$$

These equations can be solved with the help of the Pekar ABC

$$\mathcal{P}_{1y} + \mathcal{P}_{2y} = 0 \tag{2.17}$$

and the analogous equation to (2.11) with $\sigma = y$.

The result for the s-polarized reflectivity is

$$r_s(\omega) = -\prod_{j=1}^{2} \frac{\beta_j - \beta_0}{\beta_j + \beta_0}, \tag{2.18}$$

which is the weak spatial dispersion limit of the result given by the microscopic theory. The wave vectors β_j ($j = 1, 2$) appearing in (2.16) are found by solving Eq. (2.2) with specified κ and ω, just as in the case of the transverse modes of the p-polarization theory.

B. Theory of the ATR experiment

Once again the cases of s- and p-polarized incident fields are considered separately. Only the results of the calculations are given since the method is a straightforward extension of Sec. II A. There are two interfaces (see Fig. 1) at which the continuity relations[20] of the Maxwell field apply.

1. *s-polarized ATR*

The ratio of the amplitudes R_0 and E_0 in the prism ($z<0$) is given by

$$A_s(\omega) = -\frac{1-\delta_s}{1+\delta_s}, \tag{2.19}$$

with

$$\delta_s = \frac{\beta_0^{(1)}}{\beta_0^{(2)}} \frac{1+r_s^{(23)}e^{i\Delta}}{1-r_s^{(23)}e^{i\Delta}}. \tag{2.20}$$

Here superscripts (1) and (2) refer to media 1 and 2 of the prism and gap regions, respectively. Thus

$$\beta_0^{(i)} = (\epsilon_i \omega^2/c^2 - \kappa^2)^{1/2}, \quad i=1,2, \tag{2.21}$$

where ϵ_i is the dielectric constant of the glass ($i=1$) and gap ($i=2$). The quantity $r_s^{(23)}$ is the reflection amplitude for the dielectric half space given by Eq. (2.18) in the case of a vacuum gap. The dimensionless quantity

$$\Delta = 2d\beta_0^{(2)} \tag{2.22}$$

measures the effective number of wavelengths across the gap and back.

2. *p-polarized ATR*

For p-polarized light incident from the prism side of the prism-gap interface the ATR amplitude is

$$A_p(\omega) = -\frac{1-\delta_p}{1+\delta_p}, \tag{2.23}$$

with

$$\delta_p = \frac{\epsilon_2}{\epsilon_1} \frac{\beta_0^{(1)}}{\beta_0^{(2)}} \left(\frac{1+r_p^{(23)}e^{i\Delta}}{1-r_p^{(23)}e^{i\Delta}}\right), \tag{2.24}$$

where $r_p^{(23)}$ is the reflection amplitude for the gap-dielectric interface given for the case of a vacuum gap by Eq. (2.13).

III. FORMULATION OF THE MICROSCOPIC THEORY

The rest of this paper is concerned with the development and application of the microscopic theory of p-polarized optical properties of a dielectric half space. For completeness we also consider the simpler s-polarized problem. Only a brief outline of the latter is given since the principal results, based on a somewhat different division of intermolecular interactions into long- and short-range parts, have been published elsewhere. There are, however, some subtleties, overlooked heretofore, that emerge from a comparison with the p-polarized theory.

Consider a semi-infinite orthorhombic crystal with one molecule per unit cell. The sites of the lattice are taken to be

$$\vec{r}_s = na_1\hat{x} + ma_2\hat{y} + la_3\hat{z}, \tag{3.1}$$

where $n, m = 0, \pm1, \pm2, \ldots$, and $l = 1, 2, 3, \ldots$. In this model the index l labels the crystal planes parallel to the surface plane $z=a_3$. The first plane has $l=1$, the second $l=2$, and so on. The coordinate system is shown schematically in Fig. 2. Note that the crystallographic, dielectric, and external coordinate axes are parallel. Furthermore we consider only external driving fields with xz as the plane of incidence. Following convention electric fields of the type $(0, E_y, 0)$ are referred to as s polarized and those of the type $(E_x, 0, E_z)$ are called p polarized.

The classical oscillator model for excitons and polaritons in molecular crystals is used here and all nonlinear processes are neglected. The notation is the same as in Ref. 15. The response of a molecule on site $\vec{r}_s$ to a monochromatic driving field with time dependence $e^{-i\omega t}$ is described by a set of oscillating dipoles $\vec{d}_{su}e^{-i\omega t}$, where u denotes the quantum transition from the ground to the uth excited state. After cancellation of the time factor the equations of motion for any aggregate of molecules arrayed on fixed sites $\vec{r}_s$ in

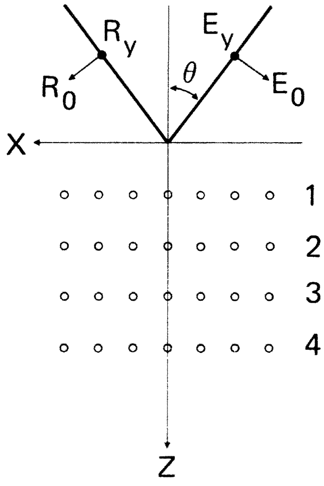

FIG. 2. Schematic diagram of the right-handed coordinate system used in the microscopic theory. Crystal planes $l=1,2,3,\ldots$, correspond to $z=a_3, 2a_3, 3a_3, \ldots$, where a_3 is the lattice constant in the z direction.

a vacuum become

$$\sum_{\sigma'} [\overleftrightarrow{1}\delta_{ss'} + 4\pi\overleftrightarrow{\alpha}_s(\omega)\cdot\overleftrightarrow{\Phi}_{ss'}(\omega)]\cdot\vec{P}_{s'} = \overleftrightarrow{\alpha}_s(\omega)\cdot\vec{E}_0(r_s)\,, \tag{3.2}$$

where $\overleftrightarrow{\alpha}_s(\omega)$ is the polarizability tensor of molecule s,

$$\overleftrightarrow{\Phi}_{ss'}(\omega) = -\left(\frac{v_c}{4\pi}\right)\left[\vec{\nabla}\vec{\nabla} + \left(\frac{\omega}{c}\right)^2\overleftrightarrow{1}\right]R^{-1}e^{i\omega R/c} \tag{3.3}$$

is a dimensionless retarded dipole-dipole interaction tensor (v_c is the unit cell volume and $R = |\vec{r}_s - \vec{r}_{s'}|$),

$$\vec{P}_s = v_c^{-1}\sum_u \vec{d}_{su} \tag{3.4}$$

is a polarization density vector defined for each site, and $\vec{E}_0(\vec{r}_s)$ is the amplitude of the driving field at site $\vec{r}_s$.

The external driving fields are monochromatic and have the form

$$\vec{E}_0(\vec{r}) = \vec{E}_0 e^{i\vec{k}\cdot\vec{r}}\,, \tag{3.5}$$

where

$$\vec{k} = \kappa\hat{x} + \beta_0\hat{z}\,. \tag{3.6}$$

If θ denotes the angle of incidence, then

$$\kappa = (\omega/c)\sin\theta\,, \tag{3.7}$$

$$\beta_0 = (\omega/c)\cos\theta\,, \tag{3.8}$$

since

$$k = |\vec{k}| = \omega/c\,. \tag{3.9}$$

Solutions of Eqs. (3.2) are sought that are periodic in the x and y directions. If we set

$$\vec{P}_s = \vec{P}_l e^{i\kappa n a_1}\,, \tag{3.10}$$

$$\overleftrightarrow{\alpha}_s = \overleftrightarrow{\alpha}_l\,, \tag{3.11}$$

Eqs. (2.2) reduce to

$$\sum_{l'} [\overleftrightarrow{1}\delta_{ll'} + 4\pi\overleftrightarrow{\alpha}_l(\omega)\cdot\overleftrightarrow{\Phi}_{ll'}(\omega;\kappa)]\cdot\vec{P}_{l'} = \overleftrightarrow{\alpha}_l(\omega)\cdot\vec{E}_0 e^{i\beta_0 l a_3}\,, \tag{3.12}$$

where

$$\overleftrightarrow{\Phi}_{ll'}(\omega;\kappa) = \sum_{n'm'} \overleftrightarrow{\Phi}_{nml,n'm'l'}(\omega)\exp[i\kappa(n-n')a_1] \tag{3.13}$$

is a two-dimensional sum of the retarded dipole interactions.

The crucial step in the formulation of the problem is the calculation of the components of the tensor $\overleftrightarrow{\Phi}_{ll'}$ and the separation of long- and short-range interactions. Formulas for the case $l = l'$ were derived in Ref. 11 as a limiting case of $l \neq l'$. Since it is the result and not the details of this calculation that are of immediate interest here, the latter are relegated to Appendix A. The lattice sums $\overleftrightarrow{\Phi}_{ll'}$ are divided into a short-range part $\overleftrightarrow{v}_{ll'}$, arising from the R^{-3} terms of $\overleftrightarrow{\Phi}_{ss'}$ that dominate in the near zone ($\omega R/c \ll 1$), and a long-range part, arising from the $R^{-1}e^{i\omega R/c}$ term that dominates for wave-zone separations ($\omega R/c \gg 1$). Explicit formulas for the long- and short-range parts are listed in Appendix A.

Now if the y axis is parallel to a principal axis of the polarizability tensors $\overleftrightarrow{\alpha}_l$ we have for s-polarized driving fields the equations

$$\sum_{l'} \{\delta_{ll'} + 4\pi\alpha_{ly}[v_{yy}(l-l') - i\tfrac{1}{2}(k^2 a_3/\beta_0)e^{i\beta_0|l-l'|a_3}]\}P_{l'y} = \alpha_{ly}E_{0y}e^{i\beta_0 l a}\,. \tag{3.14}$$

There is one equation for each $l = 1, 2, 3, \ldots$. These equations have been derived and discussed before. However, in previous work the κ and ω/c dependence of $v_{yy}(l-l')$ has not been investigated.

The equations for p-polarized driving fields are more complex because the x and z components of the material fields are coupled together. If $\overleftrightarrow{\alpha}_{\parallel}$ is the second rank tensor made up from the x and z components of $\overleftrightarrow{\alpha}_l$, then the equations for the system driven by a p-polarized external field are

$$\begin{aligned}\sum_{l'} \Big(\overleftrightarrow{1}\delta_{ll'} + 4\pi\overleftrightarrow{\alpha}_{l\parallel}\cdot\{&\hat{x}\hat{x}[v_{xx}(l-l') - \tfrac{1}{2}i a_3\beta_0 e^{i\beta_0|l-l'|a_3}] + (\hat{x}\hat{z}+\hat{z}\hat{x})i\,\mathrm{sgn}(l-l')(1-\delta_{ll'})[v_{xz}(l-l') + \tfrac{1}{2}a_3\kappa e^{i\beta_0|l-l'|a_3}] \\ &+ \hat{z}\hat{z}[v_{zz}(l-l') - i\tfrac{1}{2}(a_3\kappa^2/\beta_0)e^{i\beta_0|l-l'|a_3}]\}\Big)\cdot\vec{P}_{l'} = \overleftrightarrow{\alpha}_{l\parallel}\cdot\vec{E}_0 e^{i\beta_0 l a_3}\,. \end{aligned} \tag{3.15}$$

Note that in Eqs. (3.14) and (3.15) the short-range interactions depend on κ and k ($= \omega/c$).

The short-range interactions $\overleftrightarrow{v}(l-l')$ are so called because they fall off very rapidly with $|l-l'|$. For planes involving small Miller indices it is often the case that these interactions are negligible for $|l-l'| > 2$. Note that the off-diagonal interactions depend on the order of l and l' through $\mathrm{sgn}(l-l')$.

The p-polarization equations are simpler in several special cases. For highly anisotropic molecules one may be able to neglect all but the one component of $\overleftrightarrow{\alpha}$ corresponding to the exciton transition closest to ω. For example, the long axis of the TCNQ^0 (tetracyanoquinodimethane) molecule is almost parallel to the (010) crystal plane.[21] Therefore, near the first singlet transition which has an enormous oscillator strength ($f \simeq 2$) the system could be modeled by setting $\alpha_{yy} = \alpha_{zz} = \text{const}$.

The second special case and the one which we pursue in this paper is the case of isotropic molecules. If we set

$$\vec{\alpha}_l = \bar{\alpha}_l \vec{1} \tag{3.16}$$

and assume $\alpha_l = \alpha$ is independent of distance from the surface plane, then the p-polarized equations become

$$\sum_{l'} \left(\left\{\delta_{ll'} + 4\pi\alpha\left[v_{xx}(l-l') - i\tfrac{1}{2}a\beta_0 e^{i\beta_0|l-l'|a_3}\right]\right\} P_{l'x} + i(1-\delta_{ll'})\,\mathrm{sgn}(l-l')4\pi\alpha\left[v_{xz}(l-l') + \tfrac{1}{2}a\kappa e^{i\beta_0|l-l'|a_3}\right]P_{l'z}\right) = \alpha E_{0x} e^{i\beta_0 l a_3}\,, \tag{3.17}$$

$$\sum_{l'} \left(\left\{\delta_{ll'} + 4\pi\alpha\left[v_{zz}(l-l') - i\tfrac{1}{2}(a\kappa^2/\beta_0) e^{i\beta_0|l-l'|a_3}\right]\right\} P_{l'z} + i(1-\delta_{ll'})\,\mathrm{sgn}(l-l')4\pi\alpha\left[v_{xz}(l-l') + \tfrac{1}{2}a\kappa e^{i\beta_0|l-l'|a_3}\right]P_{l'x}\right) = \alpha E_{0z} e^{i\beta_0 l a_3}\,. \tag{3.18}$$

In passing we note that to neglect the dependence of α on l means that the theory cannot be used to study surface-exciton states arising because of site-shift induced changes in the polarizability. Evidence for the existence of the excitons has been reported for some organic crystals and some rare-gas solids.[22-26]

IV. GENERAL SOLUTION OF THE MICROSCOPIC EQUATIONS

In this section we outline how the solutions of the microscopic equations (3.14), (3.17), and (3.18) are obtained. Detailed formulas for interactions $\vec{v}(l-l')$ of arbitrary range are not given since they are long and cumbersome. Instead we focus on casting the equations that determine the optical properties into a form that renders the physics more transparent. The equations of motion are readily solved for some special cases and this is done explicitly in the sections following this one.

A. *p* polarization

For notational simplicity we set $a_3 = a$. To solve the p-polarized equations (3.17) and (3.18) we set

$$P_{lx} = \sum_j \mathcal{P}_{jx} e^{i\beta_j l a}\,, \tag{4.1}$$

$$P_{lz} = \sum_j \mathcal{P}_{jz} e^{i\beta_j l a}\,. \tag{4.2}$$

The number of modes $\mathcal{P}_{j\sigma}$ appearing in (4.1) is fixed by the range of the interactions $\vec{v}(l-l')$, as will become apparent later. The sums

$$S_j(l) = \sum_{l'=1}^{\infty} \exp[i(\beta_j l' + \beta_0|l-l'|)a]\,, \tag{4.3}$$

$$S_j'(l) = \sum_{l'=1}^{\infty} (1-\delta_{ll'})\,\mathrm{sgn}(l-l')\exp[i(\beta_j l' + \beta_0|l-l'|)a] \tag{4.4}$$

that arise in Eqs. (3.17) and (3.18) as a result of substitutions (4.1) and (4.2) have the values

$$S_j(l) = \frac{i\sin(\beta_0 a)e^{i\beta_j l a}}{\cos(\beta_j a) - \cos(\beta_0 a)} - \frac{e^{i\beta_0 l a}}{1 - e^{i(\beta_0 - \beta_j)a}}\,, \tag{4.5}$$

$$S_j'(l) = \frac{i\sin(\beta_j a)e^{i\beta_j l a}}{\cos(\beta_j a) - \cos(\beta_0 a)} - \frac{e^{i\beta_0 l a}}{1 - e^{i(\beta_0 - \beta_j)a}}\,. \tag{4.6}$$

They differ solely in the replacement of β_0 by β_j in the argument of the sine function.

Next we group together terms that are proportional to $e^{i\beta_j l a}$ and $e^{i\beta_0 l a}$, and separately set them equal to zero. In a sense we are using the idea expressed by the Oseen extinction theorem, for the fields inside the medium propagate with material wave vectors β_j and not the vacuum value β_0. After separating vacuum from material terms we obtain four equations. The equations containing $e^{i\beta_j l a}$ as factors are

$$\sum_j e^{i\beta_j l a}\left\{\left[1 + 4\pi\alpha\left(t_{xx}(\beta_j;l) + \frac{\frac{1}{2}a\beta_0\sin(\beta_0 a)}{\cos(\beta_j a) - \cos(\beta_0 a)}\right)\right]\mathcal{P}_{jx} + 4\pi\alpha\left(t_{xz}(\beta_j;l) - \frac{\frac{1}{2}a\kappa\sin(\beta_j a)}{\cos(\beta_j a) - \cos(\beta_0 a)}\right)\mathcal{P}_{jz}\right\} = 0\,, \tag{4.7}$$

$$\sum_j e^{i\beta_j l a}\left\{\left[1 + 4\pi\alpha\left(t_{zz}(\beta_j;l) + 1 + \frac{\frac{1}{2}a\kappa^2\sin\beta_0 a}{\beta_0[\cos(\beta_j a) - \cos(\beta_0 a)]}\right)\right]\mathcal{P}_{jz} + 4\pi\alpha\left(t_{xz}(\beta_j;l) - \frac{\frac{1}{2}a\kappa\sin(\beta_j a)}{\cos(\beta_j a) - \cos(\beta_0 a)}\right)\mathcal{P}_{jx}\right\} = 0\,. \tag{4.8}$$

Here we have used the notation

$$t_{\sigma\sigma}(\beta_j;l)+\delta_{z\sigma}=\sum_{l'=0}^{\infty}v_{\sigma\sigma}(l-l')e^{i\beta_j(l'-l)a} \tag{4.9}$$

for $\sigma=x,z$, and

$$t_{xz}(\beta_j;l)=i\sum_{l'=1}^{\infty}\operatorname{sgn}(l-l')v_{xz}(l-l')e^{i\beta_j(l'-l)a}\,. \tag{4.10}$$

Since the $v(l-l')$ are two-dimensional sums, the new sums are three dimensional and run over all of the semi-infinite lattice. Note that t_{zz} is defined differently from t_{xx} in order (see later) to achieve a complete separation of the macroscopic optical field.

The two equations containing $e^{i\beta_0 la}$ as a factor are not independent; they are proportional to

$$i2\pi ak\sum_j\frac{\mathcal{P}_{jx}-(\kappa/\beta_0)\mathcal{P}_{jz}}{1-e^{i(\beta_0-\beta_j)a}}=E_0\,, \tag{4.11}$$

where E_0 is the magnitude of the driving field. This last result is the analog for a discrete lattice of the Oseen extinction theorem. It is the relation between $\mathcal{P}_{j\sigma}$ and E_0 that holds if the electric fields felt by the molecules depend only on the material wave vectors β_j and not the vacuum wave vector β_0.

To complete the solution we must derive the equations that determine both the number and form of the β_j and the Fourier-like amplitudes $\mathcal{P}_{j\sigma}$ $(\sigma=x,z)$. To this end we assume that the short-range interactions $\overleftrightarrow{v}(l-l')$ vanish whenever $|l-l'|>L$. Therefore, the lattice sums $t_{\sigma\sigma'}(\beta_j;l)$ are independent of l for $l\geqslant L+1$. In the $l\geqslant L+1$ region the coefficients of $e^{i\beta_j la}$ are independent of l and since the β_j are independent functions we have

$$\left[1+4\pi\alpha\left(t_{xx}(\beta_j)+\frac{\frac{1}{2}a\beta_0\sin(\beta_0a)}{\cos(\beta_ja)-\cos(\beta_0a)}\right)\right]\mathcal{P}_{jx}+4\pi\alpha\left(t_{xz}(\beta_j)-\frac{\frac{1}{2}a\kappa\sin(\beta_ja)}{\cos(\beta_ja)-\cos(\beta_0a)}\right)\mathcal{P}_{jz}=0\,, \tag{4.12}$$

$$\left[1+4\pi\alpha\left(t_{zz}(\beta_j)+1+\frac{\frac{1}{2}(a\kappa^2/\beta_0)\sin(\beta_0a)}{\cos(\beta_ja)-\cos(\beta_0a)}\right)\right]\mathcal{P}_{jz}+4\pi\alpha\left(t_{xz}(\beta_j)-\frac{\frac{1}{2}a\kappa\sin(\beta_ja)}{\cos(\beta_ja)-\cos(\beta_0a)}\right)\mathcal{P}_{jx}=0\,. \tag{4.13}$$

The condition that $\mathcal{P}_{j\sigma}$ have a nontrivial solution is a 2×2 determinant set equal to zero, and is equivalent to a polynomial of degree $2L+1$ in $\cos(\beta_ja)$. The form of the determinants is the same for all j so that the roots of this polynomial can, in principle, be solved for $\cos(\beta_ja)$ and hence for β_j. Since the fields $P_{l\sigma}$ are bounded inside the crystal, we must select wave vectors β_j with positive imaginary parts. Note that the number of modes in the case of p polarization is $2L+1$, in contrast to $L+1$ for the corresponding case of s polarization.

Once the set $\{\beta_j\}$ has been determined the amplitudes $\mathcal{P}_{j\sigma}$ must be found. To do this we use Eqs. (4.11)–(4.13) and Eqs. (4.7) and (4.8) for the surface-layer region corresponding to the set of planes with $l=1,2,\ldots,L$. Before proceeding to the calculation of the polarization amplitudes and the optical properties we make the connection between Eqs. (4.12) and (4.13) and the Fresnel equation for a spatially dispersive continuous medium. This will allow us to identify the group of terms that corresponds to the dielectric tensor.

1. Dielectric tensor

It is convenient to introduce a tensor, which we shall call the dielectric tensor, by means of the definition

$$[\overleftrightarrow{\epsilon}(K_j,\omega)-\overleftrightarrow{1}]^{-1}_{\sigma\sigma'}=(4\pi\alpha)^{-1}[\delta_{\sigma\sigma'}+4\pi\alpha t_{\sigma\sigma'}(\beta_j)]\,, \tag{4.14}$$

where

$$\vec{\mathrm{K}}_j=\kappa\hat{x}+\beta_j\hat{z}\,. \tag{4.15}$$

Equations (4.12) and (4.13) can now be written more compactly as

$$\sum_{\sigma'}[(\overleftrightarrow{\epsilon}-\overleftrightarrow{1})^{-1}_{\sigma\sigma'}+M_{\sigma\sigma'}]\mathcal{P}_{j\sigma'}=0\,, \tag{4.16}$$

where $M_{\sigma\sigma'}$ is the matrix of trigonometrical factors which occur inside the square brackets along with the sum $t_{\sigma\sigma'}(\beta_j)$ of short-range interactions.

Our identification of the dielectric tensor is supported by the following observation. In the limit of weak spatial dispersion, where $|a\beta_j|\ll1$ for all j, the matrix $\overleftrightarrow{\mathrm{M}}$ simplifies to

$$M_{xx}=-\beta_0^2(\beta_j^2-\beta_0^2)^{-1}\,, \tag{4.17}$$

$$M_{xz}=M_{zx}=\kappa\beta_j(\beta_j^2-\beta_0^2)^{-1}\,, \tag{4.18}$$

$$M_{zz}=1-\kappa^2(\beta_j^2-\beta_0^2)^{-1}\,, \tag{4.19}$$

which is clearly independent of the interplane spacing a $(=a_3)$. If we use

$$\beta_j=(K_j^2-\kappa^2)^{1/2}\,, \tag{4.20}$$

then straightforward manipulation of (4.16) yields

$$\det|(\omega/c)^2\overleftrightarrow{\epsilon}(\vec{\mathrm{K}}_j,\omega)-K_j^2(\overleftrightarrow{1}-\hat{K}_j\hat{K}_j)|=0\,. \tag{4.21}$$

This has the same form as the Fresnel equation for a spatially dispersive medium of infinite extent[27] and supports our identification of the dielectric tensor by Eq. (4.14).

Comparing $\vec{K}_j$ with $\vec{k}$, Eq. (3.6), we see that β_0 has been replaced by β_j whereas κ has not been changed since it is determined by the periodic boundary condition along x.

Equation (4.14) is an important result since it shows that in the case of p polarization there is no simple expression for the dielectric function of a discrete lattice of isotropic molecules. Furthermore, it indicates that to treat spatial dispersion phenomena correctly the κ and ω dependence of the lattice sums $t_{\sigma\sigma'}$ must be considered very carefully.

In the limit of weak spatial dispersion $|aK_j| \ll 1$, the wave vectors β_j corresponding to any phenomenological dielectric function are found by inserting a specified $\overleftrightarrow{\epsilon}(\vec{K}, \omega)$ into Eq. (4.21) and solving the resulting polynomial for the set of roots $\{\beta_j\}$ with positive imaginary parts.

Next we show why the term $\delta_{\sigma z}$ was written separately in Eq. (4.9). Returning to Eq. (3.2) we note that for a lattice periodic along all three axes the propagating modes have frequencies and wave vectors $\vec{K}$ satisfying

$$\det|\overleftrightarrow{1} + 4\pi\alpha(\omega)\overleftrightarrow{\Phi}_{\vec{K}}(\omega)| = 0 , \tag{4.22}$$

where

$$\overleftrightarrow{\Phi}_{\vec{K}}(\omega) = \sum_R \overleftrightarrow{\Phi}_{ss'}(\omega)e^{i\vec{K}\cdot\vec{R}} . \tag{4.23}$$

This lattice sum can be evaluated by a modification of Ewald's method.[28] The long-range part is readily calculated by transforming (see Appendix C) the three-dimensional lattice sum of $R^{-1}e^{ikR}$ to the corresponding reciprocal sum and performing the differentiations, e.g., see Eq. (3.3), to generate $\overleftrightarrow{\Phi}_{\vec{K}}(\omega)$. The long-range part is

$$(\vec{K}\vec{K} - \overleftrightarrow{1}k^2)/(K^2 - k^2) . \tag{4.24}$$

The $\sigma\sigma'$ components of this tensor are the same as the optical parts of the matrix M in Eq. (4.16). The reason for defining t_{zz} different from t_{xx} in Eq. (4.9) is now clear, for without separating $\delta_{z\sigma}$ the zz components of M and (4.24) would not be equal.

Since Eqs. (4.16) and (4.22) are equivalent, we may write

$$\overleftrightarrow{\Phi}_{\vec{K}}(\omega) = \overleftrightarrow{t}(\kappa, \beta; \omega) + \left(\frac{\vec{K}\vec{K} - k^2\overleftrightarrow{1}}{K^2 - k^2}\right), \tag{4.25}$$

where $\vec{K} = \kappa\hat{x} + \beta\hat{z}$, and β is a member of the set $\{\beta_j\}$, $j = 1, 2, \ldots, 2L+1$. The components of $\overleftrightarrow{t}$ are defined by Eqs. (4.9) and (4.10) or by the "Ewald" formula[28,29] for $\overleftrightarrow{\Phi}_{\vec{K}}(\omega)$.

The Ewald formulas for $\overleftrightarrow{\Phi}_{\vec{K}}(\omega)$ may be used to generate expansions for the components of $\overleftrightarrow{t}$ valid near the center of the Brillouin zone. For a cubic crystal a straightforward expansion yields

$$t_{xx}(\vec{K}, \omega) = t(0, \omega) + \tfrac{1}{2}(\kappa^2 J_1 + \beta^2 J_2) , \tag{4.26}$$

$$t_{zz}(\vec{K}, \omega) = t(0, \omega) + \tfrac{1}{2}(\beta^2 J_1 + \kappa^2 J_2) , \tag{4.27}$$

$$t_{xz}(\vec{K}, \omega) = \tfrac{1}{2}\kappa\beta J_3 . \tag{4.28}$$

Here J_i $(i = 1, 2, 3)$ are functions of frequency ω, and $t(0, \omega)$ is the common value of the diagonal components of $\overleftrightarrow{t}$ at the center of the Brillouin zone. For a cubic crystal $t(0, 0) = -\tfrac{1}{3}$.

Using these relations the components of $\overleftrightarrow{\epsilon}(\vec{K}, \omega)$ are found to be given by

$$\epsilon_{xx}(\vec{K}, \omega) = \epsilon_0(\omega) + \tfrac{1}{2}[\epsilon_0(\omega) - 1]^2(J_1\kappa^2 + J_2\beta^2) , \tag{4.29}$$

$$\epsilon_{zz}(\vec{K}, \omega) = \epsilon_0(\omega) - \tfrac{1}{2}|\epsilon_0(\omega) - 1]^2(J_1\beta^2 + J_2\kappa^2) , \tag{4.30}$$

$$\epsilon_{xz}(\vec{K}, \omega) = -\tfrac{1}{2}[\epsilon_0(\omega) - 1]^2 J_3\kappa\beta . \tag{4.31}$$

These relations are in agreement with the form of quite general expressions derived from causal and symmetry arguments for a crystal with weak spatial dispersion.[27]

The relations show that in general the dielectric tensor $\overleftrightarrow{\epsilon}(\vec{K}, \omega)$ is neither diagonal nor proportional to a single scalar function. In general, for a cubic crystal there are three independent parameters to deal with. This makes even the theory for cubic crystals fairly complex and it is highly desirable to introduce a set of approximations to give a simple model. From Eqs. (4.29)–(4.31) we note that $\overleftrightarrow{\epsilon}(\vec{K}, \omega)$ becomes diagonal if we set $J_1 = J_2$ and $J_3 = 0$. We call this limit the simple isotropic limit.[30] In this limit

$$\overleftrightarrow{\epsilon}(\vec{K}, \omega) = \epsilon(K, \omega)\overleftrightarrow{1} , \tag{4.32}$$

where

$$\epsilon(\vec{K}, \omega) = 1 + \frac{4\pi\alpha(\omega)}{1 + 4\pi\alpha(\omega)t(\vec{K}, \omega)} \tag{4.33}$$

with

$$t_{\sigma\sigma'}(\vec{K}, \omega) = \delta_{\sigma\sigma'}[t(0, \omega) + \tfrac{1}{2}K^2 J] . \tag{4.34}$$

We emphasize that this is really a mathematical model with no basis in reality for real cubic crystals. However, this does not entirely invalidate its usefulness for as we shall see later it leads to a soluble system of equations which lends considerable insight into the effect of spatial dispersion on the optical properties.

2. *Equations of motion in the surface planes*

The surface region was defined as the set of crystal planes for which $l = 1, 2, \ldots, L$. If we assume the bulk-region equations (4.12) and (4.13) to hold for all l, then Eqs. (4.7) and (4.8) for $l = 1, 2, \ldots, L$ represent auxiliary conditions that we must impose on the amplitudes $\mathcal{P}_{j\sigma}$ in order to describe correctly the behavior of $P_{l\sigma}$ and $E_\sigma(la)$ in the surface region. These auxiliary equations may be written in the form

$$\sum_{j=1}^{2L+1} e^{i\beta_j la}[\Delta t_{xx}(l)\mathcal{P}_{jx}+\Delta t_{xz}(l)\mathcal{P}_{jz}]=0\,, \qquad (4.35a)$$

$$\sum_{j=1}^{2L+1} e^{i\beta_j la}[\Delta t_{xz}(l)\mathcal{P}_{jx}+\Delta t_{zz}(l)\mathcal{P}_{jz}]=0\,, \qquad (4.35b)$$

where $l=1,2,\ldots,L$ and

$$\Delta t_{\sigma\sigma'}(l)=t_{\sigma\sigma'}(\beta_j;l)-t_{\sigma\sigma'}(\beta_j)\,. \qquad (4.36)$$

Starting with $l=L$ we find

$$\sum_{j=1}^{2L+1} \mathcal{P}_{j\sigma}=0\,, \quad \sigma=x,z\,. \qquad (4.37)$$

For $l=L-1, L-2, \ldots, 2, 1$, Eqs. (3.35) give results differing from (4.37) by the presence of the phase factor $e^{i\beta_j(l-L)a}$. Thus Eqs. (4.35a) and (4.35b) are equivalent to the following set of auxiliary conditions to be satisfied by the amplitudes $\mathcal{P}_{j\sigma}$:

$$\sum_{j=1}^{2L+1} \mathcal{P}_{j\sigma}e^{i\beta_j la}=0\,, \quad l=0,1,\ldots,-L+1 \qquad (4.38)$$

for $\sigma=x$ and z. These conditions are analogous to those found by Mahan and Obermair in the problem of reflection at normal angles of incidence.

3. p-polarized reflection power

In this section a general formula for the reflectivity is derived. Consider a point $z=la$ $(l<0)$ outside the crystal. The total field is

$$E_x(la)=E_{0x}e^{i\beta_0 la}-2\pi a\sum_{l'=1}^{\infty}\sum_{G}[(g_x^2-k^2)P_{l'x} + ig_x\gamma_g\,\mathrm{sgn}(l-l')P_{l'x}] \times\gamma_g^{-1}e^{-\gamma_g|l-l'|a}\,. \qquad (4.39)$$

For $|l|\gg 1$ all but the $G=0$ component is negligible. Next we substitute Eqs. (4.1) and (4.2) for $P_{l\sigma}$ and after completing the sum over planes l' find

$$E_x(la)=E_{0x}e^{i\beta_0 la}+R_0\cos\theta e^{-i\beta_0 la}\,, \qquad (4.40)$$

where

$$R_0=i2\pi ak\sum_j\left(\mathcal{P}_{jx}+\frac{\kappa}{\beta_0}\mathcal{P}_{jz}\right)\frac{e^{i(\beta_0+\beta_j)a}}{1-e^{i(\beta_0+\beta_j)a}} \qquad (4.41)$$

is the reflection amplitude. A similar calculation for the z component of the total field yields

$$E_z(la)=E_{0z}e^{i\beta_0 la}+R_0\sin\theta e^{-i\beta_0 la}\,. \qquad (4.42)$$

The p-polarized reflectivity

$$r_p(\omega)=R_0/E_0 \qquad (4.43)$$

can be calculated for a fixed external frequency ω, and angle of incidence θ, by solving Eqs. (4.11), (4.16), and (4.38) for β_j and $\mathcal{P}_{j\sigma}$, and substituting the results into Eqs. (4.41) and (4.43). Rather than attempting this for the general case we prefer to confine our interest to some physically illuminating cases. The p-polarized reflection power is obtained by squaring the modulus of $r_p(\omega)$.

4. Summary of the p-polarized solution

At this point it is convenient to summarize the equations determining the amplitudes $\mathcal{P}_{j\sigma}$ and their wave vectors β_j for the problem of p-polarized polariton states. The bulk region supplies

$$\sum_{\sigma'}[(\vec{\epsilon}-\vec{1})^{-1}_{\sigma\sigma'}+M_{\sigma\sigma'}]\mathcal{P}_{j\sigma'}=0\,, \qquad (4.16)$$

which is used to determine the $2L+1$ values of β_j with positive imaginary parts and to relate $\mathcal{P}_{jz}$ to $\mathcal{P}_{jx}$. The surface auxiliary conditions on $\mathcal{P}_{j\sigma}$ from Sec. IV A2 are

$$\sum_j \mathcal{P}_{j\sigma}e^{i\beta_j la}=0, \quad l=0,1,2,\ldots,-L+1\,. \qquad (4.38)$$

The final equation relating $\mathcal{P}_{j\sigma}$ to the amplitude of the driving field, representing the extinction of vacuum fields at lattice sites, is

$$i2\pi ak\sum_j\frac{\mathcal{P}_{jx}-(\kappa/\beta_0)\mathcal{P}_{jz}}{1-e^{i(\beta_0-\beta_j)a}}=E_0\,. \qquad (4.11)$$

B. *s* polarization

The equations of motion for s polarization are given by (3.14). To solve these equations we set $\alpha_{ly}=\alpha$ and

$$P_{ly}=\sum_j \mathcal{P}_{jy}e^{i\beta_j la}\,. \qquad (4.44)$$

The number and nature of the wave vectors β_j are not the same as for the p-polarized problem. It was demonstrated in Refs. 11 and 13 that there are $L+1$ modes. The equations determining the modes are

$$[(\epsilon_{yy}-1)^{-1}+M_{yy}]\mathcal{P}_{jy}=0\,, \qquad (4.45)$$

$$\sum_j \mathcal{P}_{jy}e^{-i\beta_j la}=0, \quad l=0,-1,-2,\ldots,-L+1\,, \qquad (4.46)$$

$$i2\pi a\beta_0\sum_j\frac{\mathcal{P}_{jy}}{1-e^{i(\beta_0-\beta_j)a}}=-E_0\,. \qquad (4.47)$$

The y component of the dielectric tensor is

$$\epsilon_{yy}(\vec{K}_j, \omega) = 1 + \frac{4\pi\alpha}{1 + 4\pi\alpha t_{yy}(\kappa, \beta_j)}, \tag{4.48}$$

where

$$t_{yy}(\kappa, \beta_j) = \sum_{l=-L}^{L} v_{yy}(l) e^{i\beta_j l a} \tag{4.49}$$

depends on κ through the two-dimensional sums $v_{yy}(l)$. For a cubic crystal and small wave vectors $|aK| \ll 1$, the lattice sum (4.45) is given by

$$t_{yy}(\vec{K}, \omega) = t(0, \omega) + \tfrac{1}{2} K^2 J_2, \tag{4.50}$$

where in the limit $\omega \to 0$ the leading term is $t(0,0) = -\frac{1}{3}$.

The long-range macroscopic field is contained in

$$M_{yy} = \frac{\frac{1}{2}\beta_0 a \sin(\beta_0 a)}{\cos(\beta_j a) - \cos(\beta_0 a)}. \tag{4.51}$$

In the limit of weak spatial dispersion $|\beta_j a| \ll 1$, so that

$$M_{yy} = \frac{\beta_0^2}{\beta_0^2 - \beta_j^2} = \frac{\cos^2\theta}{1 - n_j^2} \tag{4.52}$$

becomes independent of the lattice constant a.

The wave vectors β_j are determined by Eq. (4.45) and the $L+1$ amplitudes $\mathcal{P}_{jy}$ are found by solving Eqs. (4.46) and (4.47). The reflectivity of the surface is

$$r_s(\omega) = -x_0^{-2} \prod_j \frac{x_j - x_0}{x_j - x_0^{-1}}, \tag{4.53}$$

where

$$x_0 = e^{-i\beta_0 a} \quad \text{and} \quad x_j = e^{-i\beta_j a}.$$

V. CRYSTAL WITH NO SPATIAL DISPERSION

The purpose of this section is to recover some well-known results for a medium with no spatial dispersion. This is done partly for completeness and partly to show that this corresponds to the case of negligible interactions $\vec{v}(l-l')$ between crystal planes ($L=0$ case). Throughout this section we assume that $|a\vec{K}| \ll 1$.

In the limit of weak spatial dispersion only one mode contributes in any significant way to expansions (4.1) and (4.2). The other modes have large $\operatorname{Im}\beta_j$ and are damped out after a short distance into the crystal. Let us assume that there is no interaction between crystal planes by taking $\vec{v}(l-l') \propto \delta_{ll'}$. If there is no interaction between planes, then there is negligible dispersion in the exciton energy for the direction perpendicular to the surface. Furthermore, since the xz component of $\vec{v}(l-l')$ is proportional to $(1-\delta_{ll'})$ [see Eq. (4.15)] the dielectric tensor reduces to $\epsilon(\omega)\overline{1}$, where

$$\epsilon(\omega) = 1 + \frac{4\pi\alpha(\omega)}{1 + 4\pi\alpha(\omega)t}. \tag{5.1}$$

Here $t = v_{xx}(0) = v_{zz}(0)$ according to the assumptions made above. [For a cubic crystal the three-dimensional lattice sum $t(0,0) = -\frac{1}{3}$. For cubic crystals $v_{xx}(0)$ is only approximately equal to $-\frac{1}{3}$.]

Since there is only one mode in expansions (4.1) and (4.2), we have

$$P_{l\sigma} = \mathcal{P}_{1\sigma} e^{-\beta_1 l a} \tag{5.2}$$

for $\sigma = x, z$. The secular equations (4.12) and (4.13) reduce to

$$\kappa \mathcal{P}_{1x} + \beta_1 \mathcal{P}_{1z} = 0 \tag{5.3}$$

and the 2×2 secular determinant of coefficients of $\mathcal{P}_{1\sigma}$ can be factorized to give

$$[n_1^2 - \epsilon(\omega)]\epsilon(\omega) = 0, \tag{5.4}$$

where the refractive index n_1 is defined by

$$\beta_1 = [n_1^2(\omega/c)^2 - \kappa^2]^{1/2} \tag{5.5}$$

and $\epsilon(\omega)$ is defined by Eq. (5.1). Equation (5.4) defines the frequency of the longitudinal mode by $\epsilon(\omega) = 0$ and the dispersion of the transverse mode by $n_1^2 = \epsilon(\omega)$. The reflectivity of the crystal is

$$r_p^{(0)}(\omega) = \frac{\beta_1 - \beta_0\epsilon}{\beta_1 + \beta_0\epsilon}, \tag{5.6}$$

which is equal to the well-known result for a crystal without spatial dispersion.

Finally, if there is no incident driving field, the κ and β_1 satisfy

$$\beta_1 + \beta_0\epsilon(\omega) = 0, \tag{5.7}$$

which is the equation determining the surface-polariton modes of an isotropic solid. This result is obtained by substitution of (4.11), with $E_0 = 0$, into the secular equations (4.12) and (4.13).

VI. SIMPLE ISOTROPIC SOLID

In this section we consider the solution of the microscopic equations in the limit of weak spatial dispersion for the case $L=1$. For the model used the solution proves to be identical with that presented in Sec. II A1 and therefore establishes a link between a continuum theory based on a particular ABC and a microscopic theory simplified by a well-defined sequence of steps.

The solid is assumed to have the bulk dielectric constant of the simple isotropic type given by Eqs. (4.32)–(4.34). For interactions with range $L=1$ only neighbor interactions between planes are permitted apart from all the intraplane interactions between molecules belonging to the same plane. In addition for the special case of the simple isotropic solid the off-diagonal interactions $v_{xz}(1)$ are zero.

For p-polarized fields there are three components with wave vectors β_j to be found by solving the determinant of coefficients of $\mathcal{P}_{j\sigma}$ [see Eq. (4.16)] set equal to zero. With the neglect of some nonzero factors this determinant can be simplified to

$$\epsilon(\vec{K}_j, \omega)[n_j^2 - \epsilon(\vec{K}_j, \omega)] = 0 . \tag{6.1}$$

This equation has the same form as (5.4) for the solid with no spatial dispersion ($L = 0$ case). In the simple isotropic model, however, the function $\epsilon(\vec{K}, \omega)$ depends upon $\vec{K}_j = \kappa\hat{x} + \beta_j\hat{z}$ as well as ω. The equation

$$\epsilon(\vec{K}_j, \omega) = 0 \tag{6.2}$$

yields one solution for β_j ($j = 3$) while

$$n_j^2 - \epsilon(\vec{K}_j, \omega) = 0 , \tag{6.3}$$

being a quadratic polynomial in n_j^2, yields two roots ($j = 1, 2$).

It is an easy exercise to show that Eq. (4.16) reduces to

$$\kappa\mathcal{P}_{jx} + \beta_j\mathcal{P}_{jz} = 0 \tag{6.4}$$

for $j = 1, 2$, the transverse modes, and to

$$\beta_j\mathcal{P}_{jx} - \kappa\mathcal{P}_{jz} = 0 \tag{6.5}$$

for $j = 3$, the longitudinal mode. The surface auxiliary conditions give

$$\sum_{j=1}^{3} \mathcal{P}_{j\sigma} = 0 , \quad \sigma = x, z \tag{6.6}$$

while the extinction condition, Eq. (4.11) reduces to

$$2\pi k \sum_{j=1}^{3} (\beta_j - \beta_0)^{-1}[\mathcal{P}_{jx} - (\kappa/\beta_0)\mathcal{P}_{jz}] = E_0 . \tag{6.7}$$

This system of equations is readily solved for the polarization amplitudes $\mathcal{P}_{j\sigma}$ and the reflectivity may then be calculated using (4.41) and (4.43). The final result for the reflectivity, without making any further approximations, is exactly the formula (2.13) obtained from the continuum theory in Sec. II A1.

To obtain the reflectivity of ordinary optics, where spatial dispersion is negligible, we simply take the limit $\beta_2, \beta_3 \to \infty$ and find the reflectivity given by Eq. (5.6) with ϵ replaced by n_1^2.

VII. OTHER MODELS

In this section we comment briefly on some more realistic and therefore, by necessity, mathematically more complicated models.

A. Cubic crystal

For a cubic crystal in which only nearest-neighbor plane interactions are important ($L = 1$ model) it is necessary to allow for nonzero t_{xz}. The determinant for the wave vectors β_j has three solutions; however, the determinant itself cannot be factored as in the case of the simple isotropic solid. From Eqs. (4.10) and (4.28) we see that t_{xz} is directly proportional to $\kappa\beta_j$ times a function that depends weakly on frequency. For $\theta \simeq 0°$ the dielectric tensor is approximately diagonal; however, the existence of the off-diagonal part cannot be neglected in this model since it is due to spatial dispersion. There is another complicating property of $\epsilon(\vec{K}, \omega)$; namely, the diagonal elements are not necessarily equal [see Eqs. (4.29) and (4.30)].

Once the three mode wave vectors β_j are determined the amplitudes $\mathcal{P}_{j\sigma}$ must be determined in order to calculate the reflection power. It can be shown that the presence of the xz component of $\vec{v}(l - l')$ ($l = 1, l' = 2$) does not change the form of Eq. (6.6). However, the proportionality constants in (6.4) and (6.5) are different,

$$\mathcal{P}_{jz} = B_j\mathcal{P}_{jx} , \tag{7.1}$$

where $j = 1, 2, 3$ and B_j is the ratio of coefficients in (4.12). A formula for the reflectivity can be derived in the way described in Sec. VI.

B. Anisotropic crystals

Suppose the molecules making up the lattice have a nondegenerate transition polarized perpendicular to the crystal surface. The equations of motion [see (3.15)] for this case are

$$\sum_{l'} \{\delta_{ll'} + 4\pi\alpha_z(\omega)[v_{zz}(l - l') - i\tfrac{1}{2}(a_3\kappa^2/\beta_0)e^{i\beta_0|l-l'|a_3}]\}P_{l'z} = \alpha_z(\omega)E_{0z}e^{i\beta_0 l a_3} . \tag{7.2}$$

This set of one-dimensional equations has a form similar to those for s-polarized waves and their solutions are readily found. Similarly, for a nondegenerate transition parallel to the surface, along x say, we have

$$\sum_{l'} \{\delta_{ll'} + 4\pi\alpha_x(\omega)[v_{xx}(l - l') - \tfrac{1}{2}ia_3\beta_0 e^{i\beta_0|l-l'|a_3}]\}P_{l'x} = \alpha_x(\omega)E_{0x}e^{i\beta_0 l a_3} . \tag{7.3}$$

The solution of these equations is obtained by the same route used for the s-polarized equations and will not be considered further. The reflectivity factorizes into separate contributions from each mode.

VIII. SURFACE POLARITONS AND ATR

The dispersion relation for surface polaritons is obtained from Eqs. (4.16), (4.38), and (4.11) by setting $E_0 = 0$ in the latter and then setting the determinant of the coefficients of $\mathcal{P}_{j\sigma}$ equal to zero. In ordinary optics surface polaritons are normal modes that cannot be excited by plane-wave fields incident from the vacuum side of the interface since their wave vectors $\kappa > \omega/c$. In a medium with spatial dispersion a bulk mode can exist for frequencies inside the stop band and therefore coupling between bulk and surface modes is expected. The stronger the dispersion in the exciton band (effective mass assumed to be positive) the greater the damping of the surface wave by the bulk.

Surface polaritons can be detected in principle by coupling to evanescent waves, as in the ATR experiment, and by coupling to vacuum electromagnetic fields through a surface that is either naturally rough or ruled like a diffraction grating.[31,32]

It is possible to set up a microscopic theory of the coupling to bulk and surface modes achieved in the ATR experiment. This may be done using the Hertz vector for an oscillating dipole in the vicinity of a planar interface. This technique has previously been used to study the effect of surface plasmons on transitions of molecules localized near a surface.[33] However, in the ATR experiment the gap between prism and dielectric surface is rarely small enough to perturb the energies of surface molecules by direct van der Waals interactions. Consequently, a microscopic theory of the ATR need not be constructed in the manner just suggested; rather it is quite sufficient to substitute into the formulas of Sec. II B an expression derived by the microscopic approach of Sec. III. In the limit of weak spatial dispersion ($|a\beta_j| \ll 1$) the simple isotropic model yields results identical with the continuum theory of Sec. II. Therefore, in the model calculations described in Sec. IX we use the continuum-theory equations to calculate the ATR spectrum.

IX. MODEL CALCULATIONS OF THE EFFECT OF SPATIAL DISPERSION ON THE OPTICAL PROPERTIES

To illustrate the use of the theory calculations have been performed using the ZnSe parameters first proposed by Maradudin and Mills. These parameters derived by fitting the reflection spectrum to an oscillator formula are representative of a number of other materials including ZnO and CdS. The lowest singlet exciton transitions in these systems are fairly weak, corresponding to oscillator strengths of approximately 0.01 and stopping bands of 10–15 cm^{-1} in width. The effective mass of the electron is around $0.8m_e$ to $0.9m_e$. We use the formulas given in the limit of weak spatial dispersion for the simple-isotropic-solid model. The parameters used are $\epsilon_0 = 8.1$, $\omega_p/\omega_T = 0.07416$, $0 \le D/c^2 \le 6.1728 \times 10^{-6}$, and $0 \le \gamma/\omega_T \le 10^{-4}$.

Calculations for the reflection power at the vacuum-dielectric interface and for the ATR at the prism-gap interface have been performed and will be described separately.

As mentioned briefly before there are some dangers in using the dielectric function (2.1a) in a microscopic theory that starts by assuming the oscillating dipoles are in vacuum. One consequence may be an incorrect treatment of how the background dielectric shields the long-range dipole interactions. This effect can be accounted for in the microscopic theory either by assuming the dipoles to be embedded in a medium with frequency-independent dielectric permeability ϵ_0, which causes a problem of how to treat the vacuum half space, or by partitioning α into a resonant and nonresonant part. We shall not pursue either of these approaches here; instead the rather cavalier approach of calculating the wave vectors with the phenomenological $\epsilon(\vec{K}, \omega)$ is adopted.

A. Reflection from the vacuum-dielectric interface

The role of spatial dispersion in reducing the reflectivity within the stopping band was first clearly demonstrated by Hopfield and Thomas.[2] In Fig. 3 this effect is shown for normal incidence ($\theta = 0°$) and zero damping for spatial dispersion $D_T = D/c^2$ ranging from zero to the value assumed for ZnSe. The background dielectric ϵ_0 and plasma frequency ω_p are the ZnSe values. For normal incidence there is no contribution to the reflectivity from the longitudinal mode; the two transverse polariton branches determine the reflectivity.

In Fig. 4 the polariton branches for $\kappa = 0$ are shown schematically for the $D_T = 0$ and $D_T > 0$ cases. The slower increase in reflection power with frequency for $D_T > 0$ shown in Fig. 3 is due to a slower increase in refractive index and the absence of the singularity in $n_1(\omega)$ for $\omega = \omega_T$. The longitudinal exciton (branch 3 in Fig. 4) occurs at

$$\omega_L^2 = \omega_T^2 + DK^2 + \omega_p^2/\epsilon_0 . \tag{9.1}$$

For $D_T = 0$ the longitudinal frequency occurs at $\omega_L = 1.000339\omega_T$ and since spatial dispersion causes only a very small shift in this position the peak reflection appears to occur at ω_L. In the $\gamma = 0$ limit the peak reflectivity for $D > 0$ occurs at the point where $n_2(\omega)$, the refractive index of the second branch of the bulk polariton spectrum, goes through zero. For $\omega < \omega_L$ this mode has a purely imaginary refractive index.

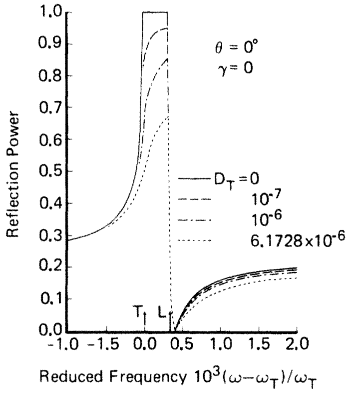

FIG. 3. Effect on the reflection power at normal incidence ($\theta = 0$) of increasing the spatial dispersion D_T from zero to the ZnSe value. The damping γ is zero.

The polarized reflection spectra for $\theta = 60^\circ$ and $D_T = 0$ and 6.1728×10^6 are shown in Figs. 5 and 6, respectively. The low p reflectivity for $\omega < \omega_T$ is due to the presence of the Brewster minimum given by $\tan\theta = n_1(\omega)$. In Fig. 7 a detail of the peak reflectivity is displayed showing discontinuities due to the wave vectors β_2 and β_3 passing through zero. For $\gamma_T \neq 0$ these edges are washed out; in particular, for $\gamma_T = 10^{-4}$ they are barely detectable. In Fig. 8 the wave vectors β_j ($j = 1, 2, 3$) are plotted against frequency. Note the separation between branch 3 (longitudinal) and branch 2 (transverse) that exists for $\kappa > 0$ and gives rise to the two separate discontinuities in the p-polarized reflection power.

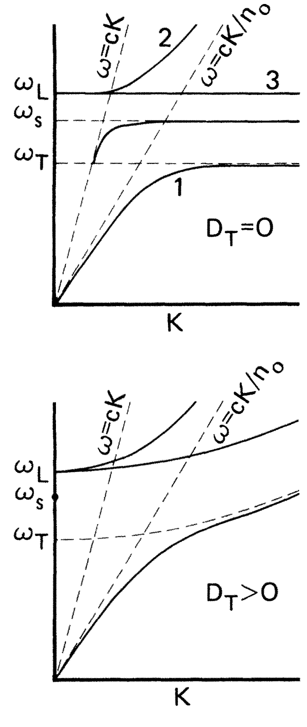

FIG. 4. Upper figure shows schematically the volume- and surface-polariton dispersion for a crystal with no spatial dispersion. The lower part shows schematically the effect of nonzero spatial dispersion ($D_T > 0$) on the volume polaritons.

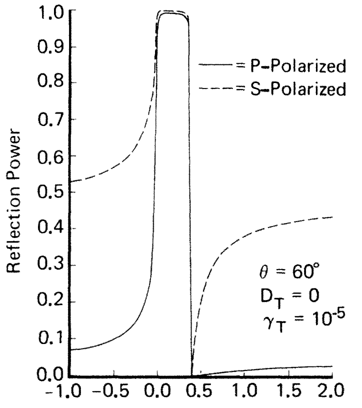

FIG. 5. s- and p-polarized reflection powers of a half space with no spatial dispersion ($D_T = 0$) in the vicinity of the stop band. The angle of incidence is 60°.

In Figs. 9 and 10 the polarized reflection spectra at $\theta = 85^\circ$ are shown for $D_T = 0$ and $D_T = 6.1728 \times 10^{-6}$. The Brewster minimum is clearly visible near ω_T. There is also a peak on the high-frequency side of the stopping band in both figures. The main effect of spatial dispersion in these low-resolution spectra is the erosion of the low-frequency edge of the reflection band. In higher-resolution calculations the p reflection contains two discontinuities similar to those visible in Fig. 7 for the $\theta = 60^\circ$ p spectrum.

At angles of incidence close to grazing the s-po-

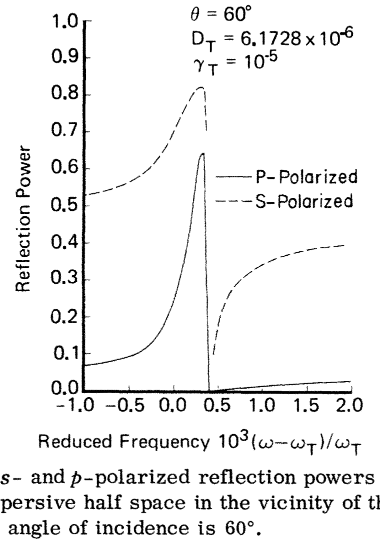

FIG. 6. s- and p-polarized reflection powers of a spatial dispersive half space in the vicinity of the stop band. The angle of incidence is 60°.

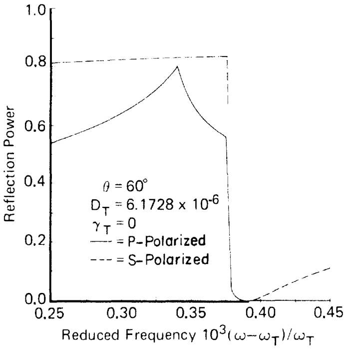

FIG. 7. Detail of the s- and p-polarized reflection powers in the vicinity of ω_L showing discontinuities due to the volume polaritons when the damping γ_T is zero.

larized reflection power is close to 1.0 for all ω except near ω_L, which there is a small dip. The p-polarized spectrum is a few percent lower with the same appearance as the spectra in Figs. 9 and 10.

In all the calculations performed no fine structure in the form of spikes or narrow minima was obtained. This is contrary to the theory of Maradudin and Mills, where a spike was found in the p-polarized reflection power which they attributed to the presence of the longitudinal exciton.

B. Attenuated-total-reflection spectra

In the absence of spatial dispersion there exists within the stopping band a normal mode referred to as a surface-polariton mode. These modes are p polarized and correspond to electromagnetic excitations confined to the surface region of the crystal. The electric field intensity of surface polaritons decays exponentially in either direction normal to the interface and they cannot be excited by photons of a vacuum half space since their energy and wave vectors cannot be simultaneously matched to any vacuum photon. The dispersion relation for a surface polariton in the limit $D_T = 0$ is

$$[\epsilon(\omega)k^2 - \kappa^2]^{1/2} + (k^2 - \kappa^2)^{1/2}\epsilon(\omega) = 0 \, .$$

If $\epsilon(\omega)$ is real and less than -1, then this equation can be solved for $\kappa > k$, yielding

$$\kappa = \left(\frac{\epsilon(\omega)}{\epsilon(\omega) - 1}\right)^{1/2} k \, .$$

This dispersion relation is displayed schematically in the top part of Fig. 4. It starts where $\omega = \omega_T$ crosses the light line and asymptotically approaches ω_S for large κ. The limiting frequency for large κ is given by

$$\omega_S^2 = \omega_T^2 + \omega_p^2/(1 + \epsilon_0)$$

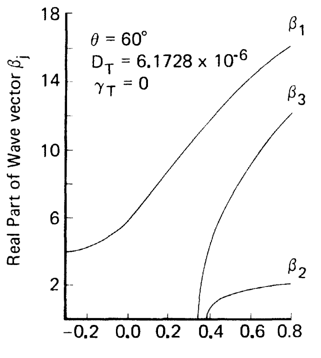

FIG. 8. Plot of the frequency dependence of the wave vectors β_j ($j = 1, 2, 3$) in the vicinity of the stop band for $\theta = 60°$ and $\gamma_T = 0$.

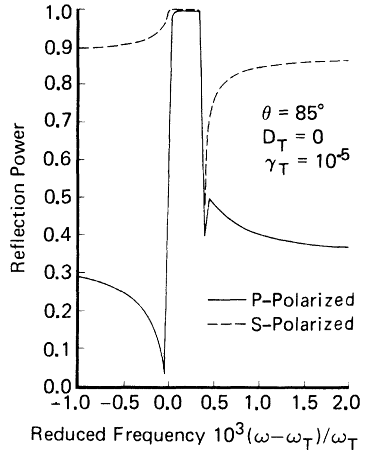

FIG. 9. s- and p-polarized reflection powers of a half space with no spatial dispersion ($D_T = 0$) in the vicinity of the stop band. The angle of incidence is 85°.

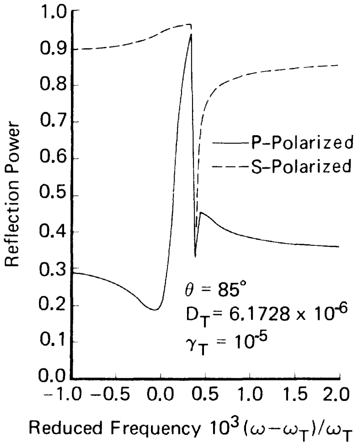

FIG. 10. s- and p-polarized reflection powers of a spatially dispersive half space in the vicinity of the stop band. The angle of incidence is 85°.

in the absence of spatial dispersion ($D_T = 0$). For the ZnSe parameters $(\omega_S - \omega_T)/\omega_T = 3.02 \times 10^{-4}$ this is close to the longitudinal frequency at $(\omega_L - \omega_T)/\omega_T = 3.39 \times 10^{-4}$.

To explore the effect of spatial dispersion on surface-polariton and ATR spectra, we have performed calculations for various angles of incidence θ for a plane-polarized electromagnetic field incident from the prism side of the prism-gap interface. These spectra have been calculated assuming the gap d between prism and dielectric satisfies

$$d\omega_T/c = 1 .$$

The magnitude of this gap was chosen to ensure reflection changes of at least several percent. The dielectric constant of the prism was taken to be $\epsilon_g = 15$, the value adopted by Maradudin and Mills.[4] For this high value the critical angle for the prism-vacuum interface is 14.963°. Figure 11 shows the effect of spatial dispersion on the p-polarized ATR spectrum for $\theta = 17°$. For small values of D_T there is a pronounced minimum due to absorption by the surface polariton. As the dispersion D_T is increased the peak near ω_T is eroded and the spectrum distorts towards that shown in Fig. 10; that is, it resembles the spectrum of the vacuum-dielectric half space at angles close to grazing incidence. Note also the increase in width and the shift to higher frequency as D_T gets larger. This effect, due to mixing with (lower frequency) transverse volume polaritons, is the subject of a separate study.

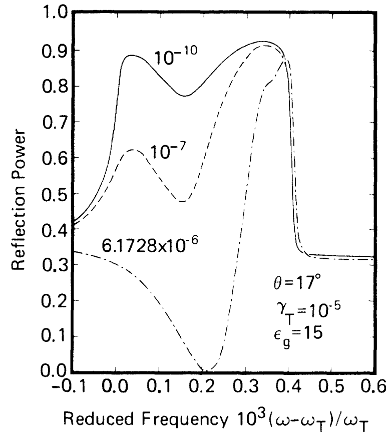

FIG. 11. p-polarized ATR spectrum for selected values of the spatial dispersion parameter, $D_T = 10^{-10}$, 10^{-7}, and 6.1728×10^{-6} (ZnSe value). The angle of incidence $\theta = 17°$ is a few degrees greater than the critical angle $\theta_c = 14.963°$ for the prism-vacuum interface. The prism-dielectric gap $d = c/\omega_T$.

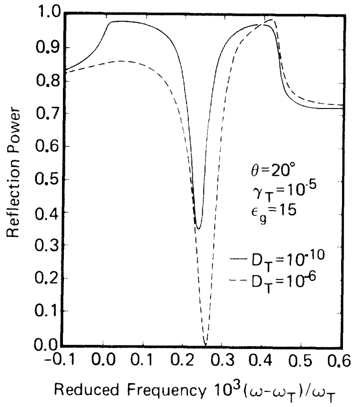

FIG. 12. p-polarized ATR spectrum at $\theta = 20°$ for two different values of the spatial dispersion parameter D_T. Note the asymmetric distortion of the minimum. The prism-dielectric gap $d = c/\omega_T$.

Calculations have been performed for the whole range of θ and values of D_T between 0 and 6.1278×10^{-6}. Two features of the calculations are worthy of comment. First it has been found that for $20° \lesssim \theta \lesssim 40°$ the effect of an increase in D_T is primarily to distort the minimum asymmetrically and to cause a small shift to higher frequencies (see Fig. 12). For much larger values of θ, where the reflection power is close to unity throughout the stop band, the minimum which is always present for $D_T = 0$ is washed out as D_T is increased. These observations admit a simple interpretation. Where dispersion is weak, coupling to lower-frequency volume modes pushes the surface mode to higher frequency. On the other hand, when the spatial dispersion is large the coupling of surface and volume polaritons results in modes that are not confined to either the surface or the bulk. These new modes have surface tails that absorb energy from the evanescent field of the prism over a wide frequency range.

APPENDIX A: CALCULATION OF $\overleftrightarrow{\Phi}_{ll'}(\omega;\kappa)$

The following integral representation is used:

$$\frac{e^{ikR}}{R} = \frac{1}{2\pi} \iint_{-\infty}^{\infty} \frac{1}{\gamma} \exp[-\gamma|z| + i(\xi x + \eta y)] d\xi\, d\eta , \tag{A1}$$

where

$$\gamma = (\xi^2 + \eta^2 - k^2)^{1/2} \tag{A2}$$

and

$$\lim_{\xi,\eta \to 0} \gamma = -ik . \tag{A3}$$

The real part of γ is positive for real ξ and real η.

With the aid of (A1) the two-dimensional lattice sum in (3.13) is converted into one over the lattice of two-dimensional reciprocal vectors G,

$$\overleftrightarrow{\Phi}_{ll'}(\omega;\kappa)=-\frac{v_c}{4\pi}(\vec{\nabla}\vec{\nabla}+k^2\overleftrightarrow{1})\frac{2\pi}{a_1a_2}\sum_G\frac{e^{i\vec{g}\cdot\vec{\rho}-\gamma_g|z|}}{\gamma_g}, \tag{A4}$$

where after differentiating with respect to $\vec{R}=(\vec{\rho},z)$ we set $\rho=0$ and $z=(l-l')a_3$. In this last equation

$$\vec{g}=\vec{\kappa}+\vec{G} \tag{A5}$$

and

$$\gamma_g=(g^2-k^2)^{1/2}. \tag{A6}$$

Equation (A4) holds only for $l\neq l'$; formulas for $l=l'$ were given in Ref. 15. The $G=0$ part is the long-range interaction and the sum of all $G\neq 0$ terms is the short-range part. This nomenclature arises because the $e^{-\gamma_g|z|}$ factor ensures that all $G\neq 0$ terms are exponentially damped, whereas the $G=0$ term is not, since

$$\gamma_0=(\kappa^2-k^2)^{1/2}=-i(k^2-\kappa^2)^{1/2}. \tag{A7}$$

In Ref. 15 an indirect argument was given for $\overleftrightarrow{\Phi}_{ll}(\omega;\kappa)$ by taking the limit as $l'\to l$. In Appendix B an explicit formula is derived for $\overleftrightarrow{\Phi}_{ll}(\omega;\kappa)$ that does not make use of this limit.

For $l\neq l'$ the lattice sums are

$$\overleftrightarrow{\Phi}_{ll'}(\omega;\kappa)=\overleftrightarrow{v}(l-l')+G=0\text{ term}. \tag{A8}$$

There are no components coupling y to x or z so that the distinction between s and p polarizations holds in the presence of spatial dispersion for the geometry of this problem provided the y axis coincides with a principal axis of the polarizability tensor α. This is no surprise since the xz plane coincides with a mirror plane of symmetry. The components of the short-range interaction are

$$v_{xx}=\tfrac{1}{2}a_3\sum_G{}'\gamma_g^{-1}(g_x^2-k^2)e^{-\gamma_g|l-l'|a_3}, \tag{A9}$$

$$v_{xz}=(1-\delta_{ll'})\tfrac{1}{2}a_3\,\mathrm{sgn}(l-l')\sum_G{}'g_xe^{-\gamma_g|l-l'|a_3}, \tag{A10}$$

$$v_{zz}=-\tfrac{1}{2}a_3\sum_G{}'\gamma_g^{-1}g^2e^{-\gamma_g|l-l'|a_3}, \tag{A11}$$

$$v_{yy}=\tfrac{1}{2}a_3\sum_G{}'\gamma_g^{-1}(g_y^2-k^2)e^{-\gamma_g|l-l'|a_3}. \tag{A12}$$

The prime signifies that the $G=0$ term is absent. The diagonal components satisfy the following sum rule:

$$\sum_\sigma v_{\sigma\sigma}=-a_3k^2\sum_G{}'\gamma_g^{-1}e^{-\gamma_g|l-l'|a_3}. \tag{A13}$$

In the limit $k=0$ where spatial dispersion is absent we see that the components of $\overleftrightarrow{v}$ reduce to static (unretarded) dipole sums satisfying the well-known sum rule

$$\sum_\sigma v_{\sigma\sigma}=0. \tag{A14}$$

APPENDIX B: FORMULA FOR $\overleftrightarrow{\Phi}_{ll}(\omega;\kappa)$

To calculate the retarded interaction between a dipole in the lth plane and all the other dipoles in the same plane it is convenient to start from the "Ewald" formula for $\overleftrightarrow{\Phi}_{\vec{K}}(\omega)$, the phase-modulated sum for a three-dimensional lattice.[28,29] If we let $a_3\to\infty$, the sum over reciprocal vector components parallel to the z axis is replaced by a standard integral. At the same time that part of the Ewald sum coming from summation over the real crystal lattice reduces to a two-dimensional sum over the lth plane only. As an example we give the result for the zz component of $\overleftrightarrow{\Phi}_{ll}$:

$$\frac{4\pi}{v_c}\hat{z}\cdot\overleftrightarrow{\Phi}_{ll}\cdot\hat{z}=\frac{\pi^{1/2}}{\eta a_1a_2}\sum_G\left\{\exp\left(\frac{-\gamma_g^2}{4\eta^2}\right)-\frac{\eta g^2}{\gamma_g}\left[1-\Phi_p\left(\frac{\gamma_g^2}{4\eta^2}\right)\right]\right\}$$
$$+\sum_\rho e^{i\vec{\kappa}\cdot\vec{\rho}}\left\{\frac{1}{\rho^3}\left[F\left(\eta\rho;\frac{k}{\eta}\right)+\frac{2\eta R}{\pi^{1/2}}e^{-\eta^2\rho^2}\right]-\frac{k^2}{\rho}F\left(\eta R;\frac{k}{\eta}\right)\right\}-\frac{4\eta^3}{3\pi^{1/2}}\left(1-\frac{k^2}{\eta^2}\right)+\tfrac{2}{3}k^3A\left(\frac{k}{\eta}\right)+i\tfrac{2}{3}k^3.$$

Here Φ_p is the probability integral and

$$F(u;v)=\frac{\pi}{\pi^{1/2}}\int_u^\infty dx\,e^{-x^2}\cos[v(u-x)],$$

$$A(u)=\frac{2}{\pi^{1/2}}\int_0^\infty dx\,e^{-x^2}\sin(ux).$$

To obtain the zz component of the short-range interaction $\overleftrightarrow{v}$ the long-range part $G=0$ must be subtracted from the sum over the reciprocal lattice.

APPENDIX C: FORMULA FOR $\overleftrightarrow{\Phi}_{\vec{K}}(\omega)$

To find the long-range (or optical field) part of the retarded dipole sum (4.23) it is not necessary to first convert the sum into a convergent Ewald sum, as done in Refs. 28 and 29. For the optical field it is sufficient to transform the lattice sum into one over the three-dimensional reciprocal lattice without dividing it into convergent sums over both the real and reciprocal spaces. Let $\vec{r}$ be a field point that does not coincide with a lattice site. Then the sum over the reciprocal lattice is simply

$$\vec{\vec{\Phi}}_{\vec{K}}(\omega)=\sum_{\vec{U}}\frac{(\vec{K}+\vec{U})(\vec{K}+\vec{U})-k^{2}\vec{\vec{1}}}{(\vec{K}+\vec{U})^{2}-k^{2}}e^{i\vec{U}\cdot\vec{r}}\,, \tag{C1}$$

where $\vec{U}$ are the reciprocal-lattice vectors and $k=\omega/c$. This result is generated by transforming the Hertz vector for the lattice to reciprocal space and then carrying out the differentiations implied in Eq. (3.3). The optical-field part of (C1) is just the $\vec{U}=0$ term.

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*An account of this work was presented at the Atlanta meeting of the American Physical Society, 1976, Abstract B012: Bull. Am. Phys. Soc. Ser. II 21, 279 (1976).

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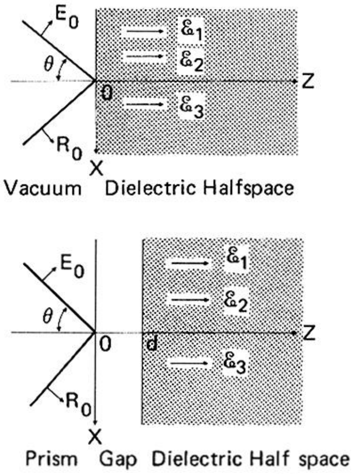

FIG. 1. Schematic representation of the right-handed coordinate system and the directions of the *p*-polarized incident and reflected electric field amplitudes for a dielectric half space without (top) and with a prism half space (bottom). For *p* polarization there are three fields $\mathcal{E}_i$ in the spatially dispersive medium.