

## Transient behavior of optically excited vapor atoms near a solid interface as observed in evanescent wave emission

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Using a cw dye laser beam normally incident on a glass-Na-vapor interface, fluorescence excitation spectra of the  $D_1$  line are measured. By observing the fluorescence transmitted into the glass above the angle of total reflection, only evanescent light emitted within about a wavelength distance from the interface is observed. The measured spectra show a cutoff on the high-frequency side which is direct evidence for the transient behavior of the induced polarization of resonantly excited vapor atoms which have collided at the solid interface.

### I. INTRODUCTION

Recently, we have reported on selective reflection spectra from a glass- (sodium) vapor interface near one of the resonance lines of the atomic vapor.<sup>1</sup> At low vapor densities such that the collisional width is much smaller than the Doppler width, the spectra exhibit features sharper than the Doppler width. This observation is at variance with the predictions of the conventional dispersion theory.<sup>2</sup> In this theory it is assumed that the induced polarization of a vapor atom depends only on the exciting field at the atom's position and on its velocity. This is certainly not true for atoms leaving the interface. These atoms have suddenly changed their velocity in the departure from the interface and have to adapt their induced polarization to the new Doppler-shifted exciting field. The adaptation occurs in a distance  $\bar{u}/\gamma$ , where  $\bar{u}$  is the most probable atomic velocity and  $\gamma$  is the homogeneous linewidth. If  $\gamma$  is much smaller than the Doppler width  $2\pi\bar{u}/\lambda$ , the adaptation occurs in a distance larger than  $\lambda/2\pi$ ,  $\lambda$  being the wavelength of the exciting field. Then the induced polarization depends nonlocally on the electric field. The resulting transient polarization behavior leads to features in the selective reflection spectra as narrow as the homogeneous linewidth  $\gamma$ .<sup>3,4</sup>

To obtain more-direct evidence for the transient polarization behavior, one would like to observe only atoms within a distance  $\lambda/2\pi$  from the interface. This can be achieved by looking at the evanescent waves emitted by the atoms. Accordingly, we have measured the fluorescence at an angle larger than the angle of total reflection, the excitation being at normal incidence. Using a single-mode cw dye laser for the excitation, the fluorescence is measured as a function of the laser wavelength. Resulting fluorescence excitation spectra for the sodium  $D_1$  line are shown in Fig. 2 as full lines. The spectra exhibit a sharp decrease on the

high-frequency side of the resonance peaks. Apparently, atoms leaving the interface contribute less than atoms moving towards the interface. This is a direct manifestation of transient polarization behavior.

In Sec. II we present a theoretical analysis of the excitation of the vapor atoms, their transient polarization behavior, and the emission of homogeneous and evanescent waves. Expressions are derived for the excitation spectra exhibiting a sharp decrease at the high-frequency side. Section III describes the experimental setup and in Sec. IV the results are presented and discussed.

### II. THEORY

The theoretical analysis gives a qualitative description of features involved in the formation of the excitation spectra. In Sec. IV it is seen that the experimental results do not allow a quantitative comparison between theory and experiment. We neglect the influence of the presence of the glass on the emission of the vapor atoms. Calculations of lifetimes and frequency shifts<sup>5</sup> indicate that this is roughly justified for atoms at a distance larger than  $\frac{1}{10}(\lambda/2\pi)$  away from the glass-vapor interface. We consider two-level atoms with transition frequency  $\omega_0$ .

#### A. Excitation of vapor atoms

A monochromatic plane electromagnetic wave in glass is normally incident on an interface between the glass (refractive index  $n$ ) and an atomic vapor. The electric field vector

$$\vec{E}^i(\vec{r}, t) = \vec{e} e^{i n k z - i \omega t} \quad (1)$$

is linearly polarized along the  $y$  direction. The wave number  $k = \omega/c$ , and  $\omega$  is near resonance to a Doppler-broadened transition. We assume a small value for the absorption so that the exciting field at the vapor atoms is essentially independent

of the presence of the vapor atoms. Then an atom that moves towards the interface has an induced polarization which, averaged over all possible collisions, is given by<sup>4</sup>

$$\vec{p}(z_a, t; u < 0) = i \frac{e^2 f}{2m_e \omega_0} \frac{e^{ikz_a - i\omega t}}{iku + i\Delta\omega + \gamma} \frac{2n}{n+1} \vec{e}, \quad (2)$$

where  $z_a$  is the position of the atom at time  $t$ ,  $u$  is the axial velocity of the atom,  $f$  is the oscillator strength,  $e$  and  $m_e$  are the electron charge and mass,  $\Delta\omega = \omega_0 - \omega$ , and  $\gamma$  is the homogeneous linewidth. The situation is different for atoms that leave the interface. Their induced polarization is given by

$$\vec{p}(z_a, t; u > 0) = \frac{ie^2 f}{2m_e \omega_0} \left( \frac{1 - \exp[-z_a(iku + i\Delta\omega + \gamma)/u]}{iku + i\Delta\omega + \gamma} \right) \times \exp(ikz_a - i\omega t) \frac{2n}{n+1} \vec{e}. \quad (3)$$

Here we have assumed that atoms depart from the interface without induced polarization. This assumption has led to a consistent interpretation of the results of selective reflection experiments.<sup>4</sup> The fluorescence of a two-level atom is determined by the upper-level population. For simplicity, we assume that atoms depart from the interface in the ground state. Atoms that leave the interface in the excited state only enhance the fluorescence for  $\omega < \omega_0$ .

#### B. Emission of evanescent waves by excited atoms

To calculate the radiation field of an electric-dipole oscillator transmitted across the interface into the glass, we use the angular spectrum representation<sup>5,7</sup> of the radiation field of the oscillator in its rest frame.

For an atom at the position  $\vec{r}_a$  at time  $t$  and with an axial velocity  $u$ , we find, since  $|ku|$ ,  $|\Delta\omega|$ , and  $\gamma$  are small compared to  $\omega$ , that the atom's radiation field is given by

$$\vec{E}(\vec{r}, t) = \frac{-i}{2\pi} \int_{-\infty}^{\infty} \int \frac{dk_x dk_y}{k_z} e^{-i\vec{k} \cdot \vec{R}} [(\vec{p} \cdot \vec{k}) \vec{k} - k^2 \vec{p}], \quad (4)$$

where  $0 < z < z_a$ ,  $\vec{R} = \vec{r} - \vec{r}_a$ ,  $\vec{k} = (k_x, k_y, k_z)$ ,  $k_z = (k^2 - k_x^2 - k_y^2)^{1/2}$ , and  $\vec{p} = \vec{p}(z_a, t; u)$ . Due to the  $1/R$  singularity of the electric-dipole field, the angular spectrum representation contains not only plane waves ( $k_x^2 + k_y^2 < k^2$ ) but also inhomogeneous or evanescent waves ( $k_x^2 + k_y^2 > k^2$ ). For detection in the  $x$ - $z$  plane far from the interface,  $kR \gg 1$ , it

is allowed to neglect the first term in square brackets of Eq. (4) since  $\vec{p}$  is perpendicular to the  $x$ - $z$  plane. The transmission of each homogeneous and evanescent wave component of (4) across the interface is calculated from the Fresnel formulas.<sup>7</sup> We obtain

$$\vec{E}(\vec{r}, t) = \frac{ik^2}{\pi} \vec{p}(z_a, t; u) \times \int_{-\infty}^{\infty} \int \frac{dk_x dk_y}{k_z + K_z} \exp[-i\vec{K} \cdot \vec{R} - i(K_z - k_z)z_a], \quad (5)$$

where  $\vec{K} = (k_x, k_y, K_z)$ ,  $K_z = (n^2 k^2 - k_x^2 - k_y^2)^{1/2}$ , and  $z < 0$ . Using the stationary-phase method,<sup>8</sup> one finds, for  $kR \gg 1$  and  $|z| \gg z_a$ ,

$$\vec{E}(\vec{r}, t) = \frac{k^2}{\tilde{R}} \frac{2K'_z}{k'_z + K'_z} \vec{p}(z_a, t; u) e^{i n k \tilde{R} + i k'_z z_a}, \quad (6)$$

where  $\vec{K}' = -\tilde{R}^{-1} \vec{R} n k$ ,  $\vec{R} = (x - x_a, y - y_a, z)$ , and  $k'_z = (k^2 - k_x'^2 - k_y'^2)^{1/2}$ .

Since  $\vec{R} \approx \vec{r}$ , we have  $\vec{K}' = (-nk \sin\Theta, 0, nk \cos\Theta)$ , where  $\Theta$  is the angle of detection. We define the critical angle  $\Theta_c = \sin^{-1}(1/n)$ . Equation (6) shows that, in accordance with the reciprocity principle, for  $\Theta < \Theta_c$  homogeneous and for  $\Theta > \Theta_c$  evanescent waves radiated by a vapor atom are transmitted across the interface.

#### C. Excitation spectra

For  $\Theta > 0$ , the radiation emitted by the different vapor atoms interferes destructively, such that the field intensity detected along the  $\Theta$  direction is proportional to the sum of the squared modulus of the detected field per atom (6) taken over all atoms. The detected light intensity is proportional to

$$I = \frac{c\rho w^2 k^4 |K'_z|^2}{|k'_z + K'_z|^2 \gamma^2} \int_0^L dz_a \int_{-\infty}^{\infty} du V(u) \times |\vec{p}(z_a, t; u)|^2 e^{-2\alpha_a/d_p}, \quad (7)$$

where  $\rho$  is the vapor density,  $V(u)$  is the velocity distribution of the vapor atoms,  $w$  is the diameter of the incident beam,  $L$  is a length which depends on the detection geometry,<sup>9</sup>  $d_p = \infty$  for  $0 < \Theta < \Theta_c$ , and  $d_p = (\lambda/2\pi)(n^2 \sin^2\Theta - 1)^{-1/2}$  for  $\Theta_c < \Theta < \frac{1}{2}\pi$ .

Below the critical angle,  $0 < \Theta < \Theta_c$ , insertion of (2) and (3) into (7), and expressing  $f$  in terms of the natural linewidth  $\gamma_N$ , yields

$$I = A (K'_z/k)^2 (K'_z + k'_z)^{-2} \gamma^{-2} (\rho w^2 L) (\gamma_N/\gamma)^2 [n/(n+1)]^2 I_{\text{inc}}.$$

Here  $I_{\text{inc}}$  is the incident light intensity and  $A$  is the dimensionless amplitude given by

$$A = \int_{-\infty}^{\infty} \frac{\gamma^2 V(u) du}{(ku + \Delta\omega)^2 + \gamma^2}. \quad (8)$$

Expression (8) displays the usual Doppler-broadened absorption spectrum. In the derivation of (8) we have used the fact that the memory length<sup>4</sup> or mean adaptation length  $l_m = \bar{u}/\gamma$  ( $\bar{u}$  is the most probable atomic velocity) is much smaller than  $L$ .

For  $\Theta = 0$ , the excitation spectrum (Appendix A) is not the usual Doppler-broadened spectrum. It shows spectral features sharper than the Doppler width since, in this case, the dipoles interfere constructively; thus  $l_m$  must be compared with the scale over which the electric field varies, i.e.,  $\lambda/2\pi$ .

Above the critical angle,  $\Theta_c < \Theta < \frac{1}{2}\pi$ , we find

$$I = \frac{1}{2} A (K_z'/k)^2 (K_z'^2 + |k_z'|^2)^{-1} \gamma^{-2} \\ \times (\rho w^2 d_p) (\gamma_N/\gamma)^2 [n/(n+1)]^2 I_{\text{inc}},$$

where

$$A = \gamma^2 \text{Im} \left( \int_{-\infty}^0 \frac{V(u) du}{(ku + \Delta\omega - i\gamma)\gamma} \right. \\ \left. + \eta \int_0^{\infty} \frac{V(u) du}{[ku + \eta(\Delta\omega - i\gamma)](\xi^{-1}ku + \gamma)} \right), \quad (9)$$

with  $\xi = kd_p$  and  $\eta = \xi/(\xi - 2i)$ . It is readily verified that for  $d_p \rightarrow \infty$ , Eq. (9) reduces to (8).

We discuss (9) for various values of  $d_p$ , the characteristic length of the emitted evanescent waves. For  $d_p \ll \lambda/2\pi$ , we have  $\eta \approx \frac{1}{2}i\xi$ ; only atoms that move towards the interface contribute significantly to the fluorescence intensity. At the low-frequency side,  $\omega - \omega_0 \ll -\gamma$ , velocity selection shows that  $A$  is described by the usual Doppler-broadened spectrum (8). At the high-frequency side,  $\omega - \omega_0 \gg \gamma$ ,  $A$  becomes a factor  $\gamma/|\Delta\omega|$  smaller. This results in a high-frequency cutoff in the excitation spectrum. For  $\omega - \omega_0 \gg \gamma$ , the main contribution to  $A$  comes from atoms with  $ku \approx (kd_p)|\Delta\omega|$ , see [Eq. (3)]. Velocity selection is absent since  $d_p \ll \lambda/2\pi$ , i.e.,  $t = d_p/\bar{u} \ll (k\bar{u})^{-1}$ . Note that the discussion for  $d_p \ll \lambda/2\pi$  is a formal one since, due to the neglect of the influence of the glass on the emission of atoms, the theoretical analysis is incomplete.

For  $d_p \gg \lambda/2\pi$ , we have  $\eta \approx 1$  and both integrals in (9) contribute to  $A$ . Velocity selection applies and the major contribution to  $A$  comes from atoms with  $ku \approx \omega - \omega_0$ . For  $\omega - \omega_0 \ll \xi\gamma$ , the characteristic length

$$d_p \gg u/\gamma \approx (\lambda/2\pi)(\omega - \omega_0)/\gamma$$

and the atoms are fully adapted to the exciting field. We find the usual Doppler-broadened spec-

trum (8). For  $\omega - \omega_0 \gg \xi\gamma$ , the atoms are not adapted ( $d_p \ll u/\gamma$ ) to the exciting field and their contribution to the fluorescence is smaller by a factor

$$\frac{d_p}{u/\gamma} \approx \frac{\xi\gamma}{\omega - \omega_0}.$$

This results in a cutoff at  $\omega - \omega_0 \approx \xi\gamma$ . When  $d_p \gg l_m = \bar{u}/\gamma$ , the cutoff occurs at a detuning  $\omega - \omega_0$  much larger than the Doppler width  $k\bar{u}$ , i.e., the cutoff shifts out of the spectrum.

### III. EXPERIMENT

The experimental setup for measuring the excitation spectra is shown schematically in Fig. 1. The light source is a cw single-mode dye laser (Spectra Physics 580A) with a spectral width of about 30 MHz. The beam splitter  $S$  provides a reference beam (II). The linearly polarized beam I is collected in the focal point of a hemispherical lens ( $n = 1.6277$ ) serving as the entrance window of the vapor cell. The collimated beam having a diameter of  $\sim 3$  mm is normally incident on the glass-vapor interface. The fluorescent light from the vapor is observed in a plane perpendicular to the polarization vector of the incident beam. The fluorescence is measured as a function of the angle  $\Theta$  with the normal, the angular resolution being about  $1^\circ$ . The excitation is on the  $D_1$  line of sodium and therefore, the fluorescent light is unpolarized. A polarizer ( $P$ ) is used to select the component that is either perpendicular or parallel to the plane of incidence. The ratio of fluorescence intensity

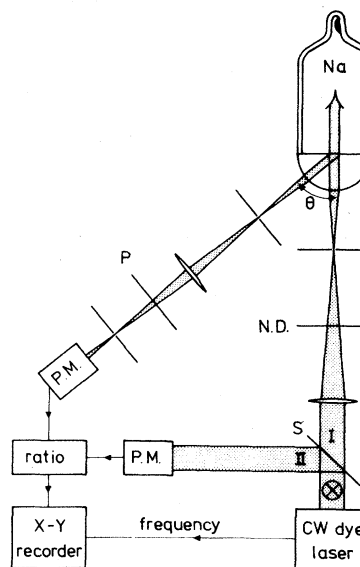


FIG. 1. Experimental setup:  $S$ , beam splitter;  $N.D.$ , neutral density filter;  $P$ , polarizer;  $P.M.$ , photomultiplier.

to excitation intensity is plotted on a chart recorder as a function of the laser frequency.

The experiments are performed with an excitation intensity of about  $1 \text{ mW/cm}^2$ . The shape of the observed spectra is found to be independent of the excitation intensity up to intensities larger than  $1 \text{ mW/cm}^2$  from which we conclude that optical pumping and saturation effects are absent in our experiments.

The cell is made of gehlenite glass<sup>10</sup> which is sodium resistant. After baking out the cell at  $500^\circ\text{C}$  for several hours at  $10^{-7}$  Torr, high-purity sodium was distilled into it. The cell is placed in a transparent oven.

The vapor density is determined from the temperature of the cold spot in the cell using known<sup>11</sup> vapor-density data. In order to avoid condensation at the entrance window its temperature is kept about 30 K above the temperature of the cold spot.

#### IV. RESULTS AND DISCUSSION

Figure 2 shows a representative set of excitation spectra taken near the  $D_1$  line for temperatures of the cold spot between 500 and 600 K. The full lines

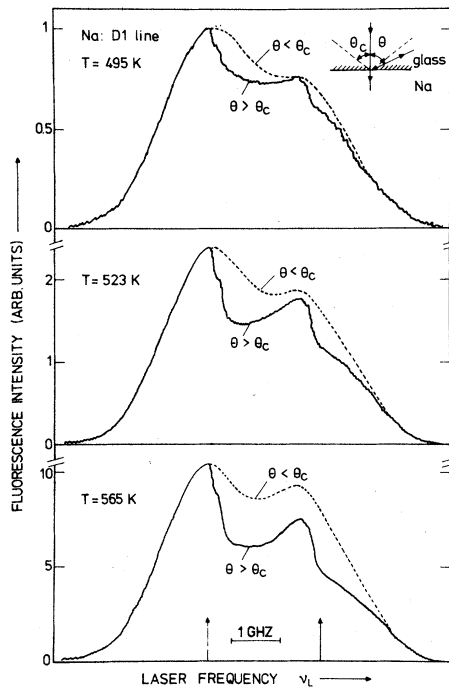


FIG. 2. Fluorescence excitation spectra of the  $D_1$  line of sodium at various cold-spot temperatures. Solid line,  $\Theta = \Theta_c + 3^\circ$ : relative intensities on vertical scale. Dotted line,  $\Theta = \Theta_c - 3^\circ$ : intensities normalized to maxima of  $\Theta > \Theta_c$  spectra. The arrows indicate the positions at which the maximum and tail amplitude are determined (see Fig. 4).

correspond to spectra obtained at an angle  $\Theta$  which is  $3^\circ$  larger than the critical angle  $\Theta_c$  ( $d_p \cong 2.7\lambda/2\pi$ ), while the dotted lines correspond to an angle which is  $3^\circ$  smaller than  $\Theta_c$ . For comparison the amplitudes of the latter spectra are reduced by a factor of about 20. The two main peaks in the spectra are a result of the hyperfine splitting 1772 MHz of the ground level.

The results obtained for  $\Theta < \Theta_c$  are understood in terms of Eq. (8). Due to the ground-level hyperfine splitting, two Doppler-broadened contributions result. At the lower vapor densities, the peak amplitudes are proportional to the vapor density and are in the ratio of 5 to 3. The peak amplitudes tend to equalize at the higher densities due to reabsorption of the fluorescent light.

For  $\Theta > \Theta_c$  both peaks in the spectra clearly show a cutoff on the high-frequency side starting slightly below the resonance frequencies which is consistent with the prediction of Eq. (9). This provides a direct proof of transient polarization behavior of atoms leaving the interface. Since the hyperfine splitting, 192 MHz, of the upper level  $3^2P_{1/2}$  is now visible on the steep slopes in the spectra, the cutoff occurs within a few hundred MHz.

The ratio of the detected intensities for perpendicular and parallel polarization is in accordance with the different index matching for TE and TM waves. As expected, the shape of the spectra is independent of the observed polarization. For  $\Theta > \Theta_c$ , the maximum amplitude of the TM spectra at 540 K is plotted in Fig. 3 as a function of the angle  $\Theta$ , together with the predicted angular dependence.<sup>12</sup>

If the excitation is not perpendicular to the in-

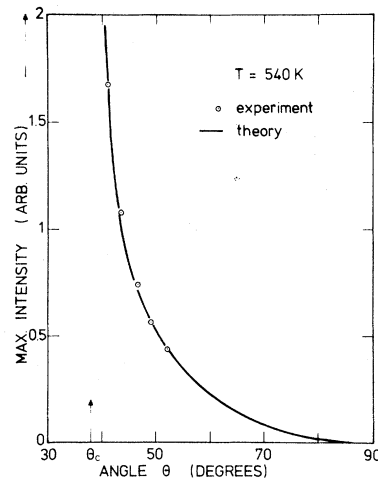


FIG. 3. Maximum intensity of the fluorescence excitation spectrum at 540 K as a function of the detection angle  $\Theta$ .

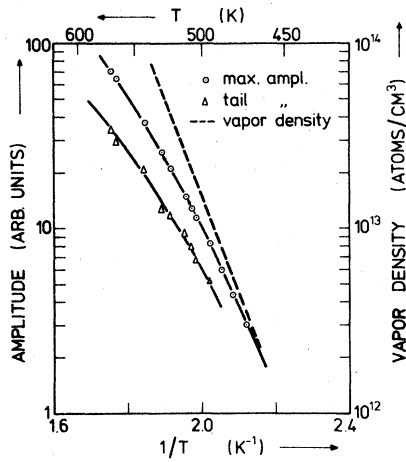


FIG. 4. Temperature dependence of maximum amplitude and tail amplitude of the excitation spectra ( $\Theta = \Theta_c + 3^\circ$ ) taken at the positions indicated by the arrows in Fig. 2. The dashed line represents the vapor density.

terface, the cutoff broadens with an increasing angle of incidence and finally disappears, since the excitation in the vapor becomes parallel to the glass wall.

The spectra in Fig. 2 for  $\Theta > \Theta_c$  show a tail at the high-frequency side, i.e., the amplitude remains larger than expected from the theoretical analysis of Sec. II. In Fig. 4, the maximum amplitude and the tail amplitude of the spectra, taken at frequencies as indicated by the arrows in Fig. 2, are plotted as a function of the inverse temperature. The dashed line represents the vapor density.<sup>11</sup> It is seen that both the temperature dependence of maximum amplitude and tail amplitude is different from the temperature dependence of the vapor density. This can be understood by assuming that the spectra are composed of two contributions: first a contribution whose amplitude is proportional to the vapor density and second a background which causes the tail. Since the amplitude of the latter is not proportional to the vapor density, and therefore most likely not due to vapor atoms, it is assumed that the tail originates from atoms adsorbed at the interface. The corresponding heat of adsorption,<sup>13</sup> which can be obtained from the temperature dependence of the tail amplitude, is then  $\sim 10$  kcal/mole. The assumption of a spectral contribution due to adsorbed atoms is

supported by an experiment in which the incident beam is at an angle with the normal larger than  $\Theta_c$ . In that case we measure a spectrum with a temperature dependence identical to that of the tail of the above spectra and a spectral shape similar to that of the bulk atoms.

In conclusion the experiments reported here provide direct evidence for transient polarization behavior of vapor atoms leaving a solid interface. The transient effects manifest themselves in a cutoff in fluorescence excitation spectra observed at an angle larger than the angle of total reflection. The cutoff is in accordance with our theoretical analysis apart from an unexpected tail at the high-frequency side. The latter might be due to a contribution of atoms adsorbed at the interface. It is surprising, however, that adsorbed atoms would have an excitation spectrum similar to that of bulk atoms. This will be the subject of further investigations.

#### APPENDIX A

For a comparison with earlier theoretical work on selective reflection,<sup>4</sup> we treat here the case  $\Theta = 0$ . The backward-scattered light of different atoms interferes constructively and the total radiated electric field amplitude  $\vec{E}_{\text{tot}}(z, t)$  is found in the following way. First, we sum with respect to atoms in an equiphase plane  $z = z_a$  of the incident field using cylindrical ( $x = 0, y = 0$ ) coordinates in that plane.<sup>14</sup> This summation eliminates the  $1/\bar{R}$  dependence of (6). Next, we sum with respect to  $z_a$  and average over the axial velocity  $u$  resulting in

$$\vec{E}_{\text{tot}}(z, t) = \frac{4\pi ik}{n+1} \rho \left( \int_0^\infty dz_a e^{ikz_a} \times \int_{-\infty}^\infty du V(u) \vec{p}(z_a, t; u) \right) e^{-ikz}. \quad (\text{A1})$$

This electric field is identical to that obtained from the earlier low vapor density treatment of selective reflection in terms of a macroscopic polarization of the atomic vapor as given in Sec. 2 of Ref. 4. The reflectivity is found by adding to  $\vec{E}_{\text{tot}}(z, t)$  the field reflected from the glass-vacuum interface.

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- <sup>7</sup>See, for example, M. Born and E. Wolf, *Principles of Optics* (Pergamon, Oxford, 1970).
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