



**HAL**  
open science

## Spectral narrowing of selective reflection

M. F. H. Schuurmans

► **To cite this version:**

M. F. H. Schuurmans. Spectral narrowing of selective reflection. *Journal de Physique*, 1976, 37 (5), pp.469-485. 10.1051/jphys:01976003705046900 . jpa-00208442

**HAL Id: jpa-00208442**

**<https://hal.science/jpa-00208442>**

Submitted on 4 Feb 2008

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Classification  
 Physics Abstracts  
 2.410

## SPECTRAL NARROWING OF SELECTIVE REFLECTION

M. F. H. SCHUURMANS

Philips Research Laboratories, Eindhoven, The Netherlands

(Reçu le 18 décembre 1975, accepté le 16 janvier 1976)

**Résumé.** — Une théorie est développée pour le rétrécissement spectral de la réflexion sélective près d'une ligne de résonance d'une vapeur atomique. Le rétrécissement est attribué au comportement transitoire des atomes qui subissent des collisions avec les parois. On calcule la réflectivité d'une interface entre du verre et une vapeur pour une distribution symétrique des vitesses atomiques dans les deux cas où les collisions entre les atomes et les parois sont diffuses ou spéculaires. Les résultats de la théorie sont comparés avec des résultats expérimentaux récents.

**Abstract.** — A theory for the spectral narrowing of selective reflection near a resonance line of an atomic vapor is developed. The narrowing is ascribed to transient polarization behaviour of vapor atoms associated with wall collisions. For normally incident light the reflectivity of a glass-vapor interface is calculated both for diffuse and for specular wall collisions and for a symmetric distribution of atomic velocities. The theoretical results are compared with recent experimental results.

1. **Introduction.** — Selective reflection of light from an atomic vapor near one of its resonance lines was first observed by Wood [1] in 1909. The phenomenon is usually analyzed in terms of the electromagnetic theory of reflection of light at the boundary of a homogeneous medium, assuming a *local* connection between the electric field and the induced polarization in that medium. In this theoretical analysis, henceforth to be referred to as the conventional dispersion theory [2], the electric field in the medium can be described by a complex refractive index. In 1954, experiments of Cojan [3] on the selective reflection from a glass-mercury vapor interface raised some doubts as to the validity of such an analysis when the sum of the natural line width  $\Delta\nu_N$  and the collisional line width  $\Delta\nu_C$  is smaller than the Doppler width  $\Delta\nu_D$  [4]. Cojan found evidence for spectral narrowing of selective reflection spectra relative to the Doppler width. Conventional dispersion theory [2] predicts a spectral width of the order of the Doppler width. Recently, spectral narrowing of selective reflection from a glass-sodium vapor interface was clearly demonstrated and measured as a function of the sodium density by Woerdman [5]. It was suggested [3, 5] that the narrowing may be ascribed to transient polarization behaviour of vapor atoms associated with wall collisions. Such a transient behaviour implies a *nonlocal* connection between the electric field and the induced polarization in the vapor and is therefore beyond the scope of the conventional dispersion theory.

It is the purpose of this paper to propose a theory for the selective reflection of light from a glass-vapor interface, accounting explicitly for the transient polarization effects associated with collisions of atoms at the interface. The optical electromagnetic field will be *normally* incident on the interface and nearly resonant with one of the resonance lines of the vapor. Cojan [3] already made a start to develop a theory of dispersion in which wall collisions are included. However, his theoretical work is limited to the case of specular wall collisions, i.e. collisions in which the induced polarization and the absolute velocity of an atom are conserved. In the temperature range where the spectral narrowing of the selective reflection occurs, wall collisions are most probably of the diffuse type, i.e. the induced polarization of an atom is lost upon a wall collision. Cojan [3] also assumed that the velocities of the vapor atoms are distributed Lorentzian instead of Maxwellian. In this paper integral representations are derived for the reflectivity of a glass-vapor interface both for diffuse and for specular wall collisions, and for a symmetric velocity distribution function of the vapor atoms. These representations are worked out in detail, partly analytically, partly numerically, for both a Lorentzian and a Maxwellian velocity distribution function. The theory is illustrated for the case of the sodium  $D_2$ -resonance line and reference is made to recent experimental results [5, 6].

The organization of this paper is as follows. In section 2, the theoretical model is outlined which describes the selective reflection from a glass-vapor

interface near a resonance line of the vapor. It is shown that for

$$\Gamma = (\Delta v_N + \Delta v_C)/\Delta v_D \lesssim 1$$

the wave propagation of the electric field in the vapor cannot be exponential, i.e. selective reflection cannot be described in terms of a complex refractive index. The reflectivity of the glass-vapor interface must then be calculated in terms of the surface admittance  $M$ , defined as the ratio of the magnetic and electric field strengths at the interface. For a vanishing vapor density  $\rho$ , the reflectivity is proportional to the real part of the surface admittance. In section 3, the surface admittance is calculated by means of perturbation theory as  $\rho \rightarrow 0$  for both specular and diffuse wall collisions. For  $\Gamma < 1$ , the resulting selective reflection spectra are narrowed relative to the Doppler width and the physical nature of that narrowing is briefly discussed. In section 4, exact integral representations for the surface admittance and for the electric field in the vapor are derived for the case of specular collisions by standard Fourier-integral techniques. The integral representation for the surface admittance is worked out analytically for the case of a Lorentzian velocity distribution function and is compared with the asymptotic results for  $\rho \rightarrow 0$  obtained in section 3. Furthermore, it is shown in section 4 and Appendix A that the electric field at large distances from the glass-vapor interface decreases more slowly than exponentially. Wiener-Hopf techniques [7] are used to derive exact integral representations for the electric field in the vapor and the surface admittance in the case that we are dealing with diffuse wall collisions. The mathematical analysis is given in Appendix B and the results are summarized in section 5. The integral representation obtained in that manner for the surface admittance is evaluated analytically for a Lorentzian velocity distribution function and numerically for a Maxwellian velocity distribution function. A comparison with the asymptotic results for  $\rho \rightarrow 0$  in section 3 is made at the end of section 5. Finally, in section 6, the theory is applied to the sodium  $D_2$ -resonance line.

**2. Theoretical model.** — Consider a system consisting of glass on one side of an interface and vapor on the other side. The interface is in the  $y$ - $z$  plane and the positive  $x$ -axis is directed towards the interior of the vapor. In the vapor, the electric light field  $E(x) \exp(-i\omega t)$  is taken in the  $y$ -direction and the magnetic field  $H(x) \exp(-i\omega t)$  in the  $z$ -direction. The velocity component of a vapor atom in the  $x$ -direction is indicated by  $u$  and will be positive for atoms moving towards the interior of the vapor.

We restrict ourselves to small field intensities. Then the polarization  $p_a$  induced by the electric field in a

fixed two-level atom is in the  $y$ -direction and satisfies [2]

$$\begin{aligned} \frac{d^2 p_a}{dt^2} + 2\gamma \frac{dp_a}{dt} + (\gamma^2 + \omega_0^2) p_a &= \\ &= \frac{e^2 f}{m} E(x) \exp(-i\omega t), \end{aligned} \quad (2.1)$$

where  $\omega_0 = 2\pi\nu_0$ ,  $\nu_0$  is the transition frequency,  $\gamma$  a damping constant,  $f$  the oscillator strength,  $e$  the electron charge,  $m$  its mass and  $x$  the position of the atom. As is well known [2], (2.1) is derived both from classical and from quantum mechanical considerations. The damping  $\gamma$  is assumed to account both for the radiation damping  $\gamma_N = \pi\Delta v_N$  and for the collisional damping  $\gamma_C = \pi\Delta v_C$ , i.e.  $\gamma = \gamma_N + \gamma_C$ . In the rotating wave approximation ( $|\omega - \omega_0| \ll \omega_0$ ) (2.1) reduces to

$$\frac{dp_a}{dt} + (\gamma + i\omega_0) p_a = \frac{ie^2 f}{2m\omega_0} E(x) \exp(-i\omega t). \quad (2.2)$$

If an atom has a velocity  $u$  then (2.2) still holds but  $d/dt$  should be considered as a total derivative, i.e.

$$d/dt = \partial/\partial t + u(\partial/\partial x).$$

We shall indicate the induced polarization of such an atom by  $p_a(x, t; u)$ , where  $x$  is the position of the atom at the time  $t$ . If

$$p_a(x, t; u) = p_a(x; u) \exp(-i\omega t)$$

then  $p_a(x; u)$  satisfies

$$\begin{aligned} \frac{d}{dx} p_a(x; u) + \left( \frac{\gamma + i\Delta\omega}{u} \right) p_a(x; u) &= \\ &= i \frac{e^2 f}{2m\omega_0 u} E(x), \end{aligned} \quad (2.3)$$

where  $\Delta\omega = \omega_0 - \omega$ . Note that  $\Delta\omega$  is negative at the high frequency side of  $\omega_0$ . The general solution of (2.3) can be written in the form :

$$\begin{aligned} p_a(x; u) = \exp \left[ - \frac{(\gamma + i\Delta\omega)x}{u} \right] \left\{ p_0(u) + \right. \\ \left. + \frac{ie^2 f}{2m\omega_0 u} \int_{x_0(u)}^x E(x') \exp \left[ \frac{(\gamma + i\Delta\omega)x'}{u} \right] dx' \right\}, \end{aligned} \quad (2.4)$$

where  $p_0(u)$  and  $x_0(u)$  are to be determined by appropriate boundary conditions. Consider first atoms that move towards the interface, i.e.  $u < 0$ . Then the assumption that  $E(x)$  and  $p_a(x; u)$  vanish for  $x \rightarrow \infty$  immediately yields :

$$\begin{aligned} p_a(x; u < 0) = - \frac{ie^2 f}{2m\omega_0 u} \times \\ \times \int_x^\infty E(x') \exp \left[ \frac{(\gamma + i\Delta\omega)(x' - x)}{u} \right] dx'. \end{aligned} \quad (2.5)$$

If a fraction  $\eta$  ( $0 \leq \eta \leq 1$ ) of the atoms collides specularly with the interface and a fraction  $1 - \eta$  diffusely, we find

$$p_a(x; u > 0) = \frac{ie^2 f}{2m\omega_0 u} \times \left\{ \eta \int_0^\infty E(x') \exp\left[-\frac{(\gamma + i\Delta\omega)(x' + x)}{u}\right] dx' + \int_0^x E(x') \exp\left[\frac{(\gamma + i\Delta\omega)(x' - x)}{u}\right] dx' \right\}. \quad (2.6)$$

Having thus determined the induced polarization of the atoms of the vapor, the macroscopic polarization of the vapor can be determined from the relation

$$P(x) = \rho \int_{-\infty}^\infty V(u) p_a(x; u) du, \quad (2.7)$$

where  $V(u)$  is the velocity distribution function of the vapor atoms. Probably the most realistic assumption is that  $V(u)$  is a Maxwellian distribution function

$$V_M(u) = \frac{1}{u_{th} \sqrt{\pi}} \exp\left[-\frac{u^2}{u_{th}^2}\right], \quad (2.8)$$

where  $u_{th} = (2k_B T/m_A)^{1/2}$  is the mean thermal velocity of the vapor atoms and  $m_A$  and  $T$  stand for the atomic mass and the absolute temperature of the vapor, respectively. The Doppler width

$$\Delta\nu_D = \pi^{-1} \sqrt{\ln 2} k u_{th} [8],$$

where  $k = \omega/c$ . In order to carry out detailed analytical calculations we shall also use the Lorentzian velocity distribution function

$$V_L(u) = \frac{1}{\pi} \frac{\bar{u}}{u^2 + \bar{u}^2}, \quad (2.9)$$

where  $\bar{u}$  is chosen such that the full widths at half maximum of  $V_M(u)$  and  $V_L(u)$  are the same, i.e.  $\bar{u} = u_{th} \sqrt{\ln 2}$ . We should note that although the total integrated probability for both  $V_M(u)$  and  $V_L(u)$  equals one,  $V_M(u)$  and  $V_L(u)$  differ considerably in shape. In fact we have

$$V_M(0) = \sqrt{\pi \ln 2} V_L(0) \approx 1.476 V_L(0)$$

whereas  $V_L(u) > V_M(u)$  for  $|u| > 1.55 \bar{u}$ .

For a given macroscopic polarization  $P(x)$ , the electric field  $E(x)$  is determined by Maxwell's equation

$$\frac{d^2 E}{dx^2} + k^2 E = -4\pi k^2 P. \quad (2.10)$$

Finally the boundary conditions for the electric field must be derived. Let the electric field strengths of the

incident and the reflected electromagnetic waves in the glass be given by

$$E_{in} \exp[ikn_{gl} x - i\omega t]$$

and

$$E_r \exp[-ikn_{gl} x - i\omega t],$$

respectively. Here,  $n_{gl}$  is the refractive index of the glass. Continuity of the electric and magnetic field strengths across the glass-vapor interface yields the conditions

$$E_{in} + E_r = E(0), \quad (2.11a)$$

$$ikn_{gl}(E_{in} - E_r) = E'(0), \quad (2.11b)$$

where the prime denotes differentiation with respect to  $x$ . For a given  $E_{in}$ , (2.5)-(2.7), (2.10) and (2.11) determine the electric field in the vapor. Introducing  $R = E_r/E_{in}$ , (2.11) can be written in the form

$$\frac{1 - R}{1 + R} = \frac{M}{n_{gl}}, \quad (2.12)$$

where the surface admittance  $M$  is given by

$$M = E'(0)/(ikE(0)). \quad (2.13)$$

From (2.12) it is seen that the surface admittance can be considered to be an effective refractive index. What is measured in selective reflection experiments is the reflectivity

$$R = |R|^2 = \left| \frac{n_{gl} - M}{n_{gl} + M} \right|^2. \quad (2.14)$$

Therefore in order to calculate the reflectivity we only need to know the values of the electric field and its gradient at the glass-vapor interface, and the value of the refractive index of the glass.

We shall now assume that the electric field in the vapor can be described by a complex index of refraction  $N(\omega)$ , i.e.

$$E(x) = E^0 \exp[ikN(\omega)x] \quad (2.15)$$

and discuss the difficulties that may arise from such an assumption. The complex quantity  $N(\omega)$  can be written in the form  $n(\omega) + i\chi(\omega)$  with real  $n$  and  $\chi$ . The nonnegative quantity  $\chi$  is usually called the attenuation index. In terms of  $n$  and  $\chi$  the absorption length is given by  $l_{abs} = (2n\chi k)^{-1}$  [8]. According to (2.5) and (2.15), the induced polarization of an atom that is moving towards the interface with velocity  $u$  corresponds to

$$p_a(x; u) = \alpha(\omega; u) E(x), \quad (2.16)$$

where the polarizability per atom

$$\alpha(\omega; u) = \frac{ie^2 f}{2m\omega_0} \frac{1}{\gamma + i\Delta\omega + ikuN(\omega)}. \quad (2.17)$$

The adaptation of the atom's polarization to the spatial variation of the electric field is expressed solely by the dependence of the polarizability per atom on the atom's velocity. If an atom has collided diffusely at the interface and moves towards the interior of the vapor with velocity  $u$ , one infers from (2.6) and (2.15) that its induced polarization is given by

$$p_a(x; u) = \alpha(\omega; u) \left\{ E^0 \exp[ikN(\omega)x] - E^0 \exp\left[-\frac{(\gamma + i\Delta\omega)x}{u}\right] \right\}. \quad (2.18)$$

The second term in the curly brackets of this relation corresponds to a damped, free (not driven by the electric field) oscillation of the dispersion electron. It describes the transient adaptation of the atom's polarization to the electric field. The essential length involved in the adaptation is the memory length  $l_m(u) = u/\gamma$ . A somewhat more detailed discussion of the adaptation will be given in section 3. It will be clear that the transient contribution to (2.18) certainly cannot be neglected if  $ku\chi > \gamma$ , i.e. if

$$u > \sqrt{\ln 2} (\Gamma/\chi) u_{th}.$$

Consider for a moment only the first term in the curly brackets of (2.18). The work performed by the electric field on an atomic oscillator moving with velocity  $u$  is then proportional to  $\omega \operatorname{Im} \alpha(\omega; u) |E(x)|^2$ , and an atom absorbs energy from the light field if

$$\operatorname{Im} \alpha(\omega; u) > 0.$$

However, for atoms with velocities  $u$  satisfying  $ku\chi > \gamma$ , the imaginary part of  $\alpha(\omega; u)$  is negative and therefore these atoms drive the electric field instead of being driven by that field. To express it differently, such atoms acquire induced polarizations which are more determined by the electric field they have felt in the past than by the present (weaker) field. Indeed the condition  $ku\chi > \gamma$  can also be written as

$$l_m(u) > 2 n(\omega) l_{abs}(\omega) \quad (2.19)$$

and  $2 n(\omega) l_{abs}(\omega) = (k\chi(\omega))^{-1}$  is the  $1/e$  decay length of the electric field in the vapor. In the case that specular wall collisions are also involved, a similar discussion applies. In conclusion, the above considerations show that the electric field in the vapor cannot be purely exponential. To calculate the reflectivity of the glass-vapor interface we have to solve the eqs. (2.5)-(2.7), (2.10) and (2.11) exactly. However, it will turn out that for  $\Gamma \gg 1$  and also in the far wings of the resonance line, the reflectivity can be calculated assuming an electric field of the form (2.15) and omitting the transient contribution

to (2.18). In this case one finds from Maxwell's eq. (2.10) that  $N$  satisfies

$$N^2 - 1 = \frac{2\pi e^2 f\rho}{m\omega_0} \int_{-\infty}^{\infty} du \frac{V(u)}{\Delta\omega + kuN - iy}. \quad (2.20)$$

This is the well-known implicit equation for the complex refractive index as derived by Voigt [9]. To first order in the density we find

$$N - 1 = \frac{\pi e^2 f\rho}{m\omega_0} \int_{-\infty}^{\infty} du \frac{V(u)}{\Delta\omega + ku - iy}, \quad (2.21)$$

which is the conventional expression for the complex refractive index, cf. Born [2]. For further reference it is useful to write this expression in the form

$$N - 1 = \tilde{K}Z(i\tilde{\Gamma} - \tilde{\Delta}) \quad (2.22)$$

for the Maxwellian velocity distribution (2.8) and

$$N - 1 = \frac{iK}{1 + \Gamma + i\Delta} \quad (2.23)$$

for the Lorentzian velocity distribution (2.9). Here we have introduced

$$K = \frac{\pi e^2 f\rho}{m\omega_0} \frac{1}{\pi \Delta v_D}, \quad (2.24)$$

$$\Delta = \Delta\omega/(\pi \Delta v_D), \quad \tilde{K} = \sqrt{\ln 2} K, \\ \tilde{\Gamma} = \sqrt{\ln 2} \Gamma, \quad \tilde{\Delta} = \sqrt{\ln 2} \Delta$$

and  $Z(\zeta)$  is the plasma dispersion function as defined by Fried and Conte [10]. From (2.21) it is seen that for  $\Gamma \gg 1$ , and also in the case  $|\Delta| \gg 1$ , the attenuation index  $\chi$  indeed has such a small value that condition (2.19) is only satisfied for extremely large atomic velocities. The quantity  $K$  will be called the optical density of the vapor. It is a measure for the number of moving atoms which by interference build up the coherent electric field in the vapor. We will assume throughout this paper  $K \ll 1$ . Then we have  $n = 1 + O(K)$  and although the number of atoms in a cubic wavelength may still be large, the negligence of the Lorentz-Lorenz correction [11] in the previous considerations is justified. To first order in  $K$  the absorption length is given by  $l_{abs} = (2k\chi)^{-1}$ , where  $\chi = \operatorname{Im} N$  satisfies (2.21).

### 3. Perturbation theory for vanishing vapor densities.

— In this section the surface admittance  $M$  is calculated by means of a perturbation expansion of the electric field in the optical density  $K$  of the vapor both for diffuse and specular wall collisions and for a symmetric velocity distribution function of the vapor atoms. In general,  $\Gamma$  will also depend on  $K$ . If no buffer gas is present and the collisions of the vapor atoms are resonance collisions, then according to

Weisskopf [12],  $\Delta v_C/\Delta v_D$  is proportional to  $K$ . A perturbation expansion with respect to  $K$  must then in general also be a perturbation expansion with respect to  $\Gamma$ . However, in this section the discussion will be limited to values of  $K$  small enough to justify neglecting the dependence of  $\Gamma$  on  $K$ , i.e. it will be assumed that  $K \ll \Gamma$ . For resonance collisions of vapor atoms and in the absence of a buffer gas this limitation implies that natural line broadening is dominant in the vapor. Then we have  $\Gamma \approx \Delta v_N/\Delta v_D$ , which is much smaller than one. Only in the presence of a buffer gas can the limitation  $K \ll \Gamma$  be satisfied for  $\Gamma$  larger than one. The inequality  $K \ll \Gamma$  implies that the mean memory length or mean free path  $l_m(u_{th})$  is much smaller than the absorption length at resonance  $l_{abs}(\omega_0)$ . From the discussion in the previous section on memory effects one infers that this is precisely the regime of densities where the conventional dispersion theory can be a good approximation. However, it will turn out to be so only for  $\Gamma \gg 1$ .

We shall start the calculations from a slightly modified version of Maxwell's eq. (2.10) :

$$\frac{d^2 E}{dx^2} + k^2(1 + 2i\varepsilon)E = -4\pi k^2 P. \quad (3.1)$$

The quantity  $\varepsilon$  is a positive infinitely small real number which acts as a convergence factor. The right hand side of (3.1) is proportional to the optical density  $K$  and will be treated as the perturbation. The unperturbed electric field in the vapor is given by

$$E_0(x) = e_0 \exp[(i - \varepsilon)kx] \quad (x \geq 0), \quad (3.2)$$

where  $e_0$  is a constant. This field corresponds to an electromagnetic wave in vacuum propagating towards positive  $x$ -values. From (2.5)-(2.7) the polarization  $P_0(x)$  induced in the vapor by that wave can be calculated. Using (3.1) the first order correction to the electric field is given by

$$E_1(x) = -4\pi k^2 \int_{-\infty}^{\infty} \bar{P}_0(x') \times \frac{e^{(i-\varepsilon)k|x-x'|}}{2(i-\varepsilon)k} dx', \quad (3.3)$$

where  $\bar{P}_0(x) = P_0(x)$  for  $x \geq 0$  and  $\bar{P}_0(x)$  for  $x < 0$  is as yet undetermined. Combining (3.2) and (3.3), the electric field can also be written in the form

$$E = \bar{e}_0 \exp[(i - \varepsilon)kx] - 4\pi k^2 \int_0^{\infty} P_0(x') \times \frac{e^{(i-\varepsilon)k|x-x'|}}{2(i-\varepsilon)k} dx' \quad (x \geq 0), \quad (3.4)$$

where

$$\bar{e}_0 = e_0 - 4\pi k^2 \int_{-\infty}^0 \bar{P}_0(x') \frac{e^{(\varepsilon-i)kx'}}{2(i-\varepsilon)k} dx'. \quad (3.5)$$

The quantity  $\bar{e}_0$  is uniquely determined by the boundary conditions (2.11). However,  $e_0$  and  $\bar{P}_0(x)$  for  $x < 0$  may be chosen arbitrarily as long as they satisfy (3.5). For the calculation of the surface admittance to first order in  $K$  such considerations are not needed. From (3.2), (3.3) and (2.13) one readily finds

$$M = 1 - \frac{4\pi ik}{e_0} \int_0^{\infty} dx P_0(x) \exp[(i - \varepsilon)kx], \quad (3.6)$$

which is independent of  $e_0$  ( $P_0 \propto e_0$ ) and  $\bar{P}_0(x)$ . In the following we put  $e_0 = 1$ . We have derived now a simple formula which relates the surface admittance  $M$  to the polarization  $P_0(x)$  induced in the vapor by a plane electromagnetic wave which propagates into the vapor and satisfies Maxwell's equations in vacuum. From (2.5) and (2.6) we find the polarization of an atom with velocity  $u$  induced by  $E_0(x)$  to be given by

$$p_{a,0}(x; u < 0) = \frac{ie^2 f}{2m\omega_0} \frac{e^{(i-\varepsilon)kx}}{iku + \gamma + i\Delta\omega}, \quad (3.7)$$

$$p_{a,0}(x; u > 0) = \frac{ie^2 f}{2m\omega_0} \left\{ \frac{\eta \exp\left(-\frac{x}{u}[\gamma + i\Delta\omega]\right)}{-iku + \gamma + i\Delta\omega} + \frac{e^{(i-\varepsilon)kx} - \exp\left(-\frac{x}{u}[\gamma + i\Delta\omega]\right)}{iku + \gamma + i\Delta\omega} \right\}. \quad (3.8)$$

Eq. (3.7) expresses the coherent response of an atom moving towards the glass-vapor interface to the electric field  $E_0(x)$ . According to (3.8) an atom which has just collided at the interface has an induced polarization

$$p_{a,0}(x = 0_+; u > 0) = \frac{ie^2 f}{2m\omega_0} \frac{\eta}{-iku + \gamma + i\Delta\omega}. \quad (3.9)$$

The atom now feels an electric field with a Doppler shift different from that before the collision. Therefore, even for  $\eta = 1$ , immediately after the collision the induced polarization no longer corresponds coherently to the electric field and in moving away from the interface it will exhibit transient polarization behaviour (eq. (3.8)) until the atom's polarization has re-established a relation with the new field similar to the one that existed between the polarization and the electric field before the collision at the interface (eq. (3.7)). Indeed, for  $x \gg l_m(u)$ , we have

$$p_{a,0}(x; u > 0) = \frac{ie^2 f}{2m\omega_0} \frac{e^{(i-\varepsilon)kx}}{iku + \gamma + i\Delta\omega}. \quad (3.10)$$

Let us now discuss the various contributions to the surface admittance. The coherent part of the pola-

rization as described by (3.7) and (3.10) results, using (2.7) and (3.6), in a contribution

$$M_{\text{coh}} = 1 + K \int_{-\infty}^{\infty} \frac{V_0(y)}{y + \Delta - i\Gamma} dy. \quad (3.11)$$

Here the dimensionless velocity distribution function

$$V_0(y = u/\bar{u}) = \bar{u}V(u).$$

The expression (3.11) for  $M_{\text{coh}}$  is equal to the conventional expression for the complex refractive index of the vapor (2.21). Therefore, in a sense all deviations from the conventional dispersion theory are entirely due to the above discussed transient polarization behaviour of vapor atoms. According to (2.7), (3.6) and (3.8) that behaviour results in a contribution to the surface admittance

$$M_{\text{trans}} = 2K \int_0^{\infty} dy y V_0(y) \left\{ \frac{\eta}{[i(y-1) - \Gamma]^2} + \frac{1}{[i(y+\Delta) + \Gamma][i(y-\Delta) - \Gamma]} \right\}. \quad (3.12)$$

The first term in the curly brackets corresponds to the destruction of the polarization  $p_{a,0}(x=0_+; u>0)$  that is left after a specular (partly if  $\eta < 1$ ) collision of an atom with velocity  $u$ . The second term in these brackets corresponds to the construction of a polarization which is coherent to the new field. The total surface admittance  $M$  equals the sum of  $M_{\text{coh}}$  and  $M_{\text{trans}}$ .

Before evaluating  $M$  for a Maxwellian or a Lorentzian velocity distribution function a somewhat more general discussion of the results obtained so far will be presented. We can write the expressions (3.11) and (3.12) for  $M_{\text{coh}}$  and  $M_{\text{trans}}$  in the form of convolution integrals. Introducing the dispersion function

$$D(y) = K/(y - i\Gamma),$$

we find

$$M_{\text{coh}} - 1 = \int_{-\infty}^{\infty} V_0(y) D(y + \Delta) dy, \quad (3.13)$$

expressing the fact that in the conventional dispersion theory collisions of atoms and motions of atoms are treated as statistically independent processes. Using partial integration one obtains from (3.12)

$$M - 1 = \int_{-\infty}^{\infty} \hat{V}_0(y) D(y + \Delta) dy, \quad (3.14)$$

where

$$\hat{V}_0(y) = \begin{cases} \eta \left[ 4V_0(y) - 2y \frac{dV_0}{dy} \right] + 2(1-\eta)V_0(y) & (y \leq 0), \\ 0 & (y > 0). \end{cases} \quad (3.15)$$

Thus  $M - 1$  is a convolution of the dispersion function  $D(y)$  and a function  $\hat{V}_0(y)$  which has a break at  $y = 0$  and vanishes for  $y > 0$ . This is quite a remarkable property as it immediately implies that  $M - 1$  contains a contribution with a spectral width smaller than the Doppler width if  $\Gamma < 1$  [5]. Moreover, it is seen that the amplitude of that spectrally narrow contribution is about twice as large for the case of specular wall collisions as it is for the case of diffuse wall collisions. We note that the contribution to the surface admittance from atoms moving towards the interface can be written in a form similar to (3.14) :

$$(M - 1)|_{u < 0} = \int_{-\infty}^{\infty} \hat{V}_0(y) D(y + \Delta) dy. \quad (3.16)$$

Here  $\hat{V}_0(y) = V_0(y)$  for  $y \leq 0$  and  $\hat{V}_0(y) = 0$  for  $y > 0$ . However, this certainly does not imply that the value of the surface admittance stems primarily from atoms moving towards the interface. For diffuse wall collisions we have  $\hat{V}_0(y) = \frac{1}{2} \hat{V}_0(y)$  and therefore atoms moving either towards or from the interface contribute equally to the surface admittance.

This section will be concluded with a further evaluation of the surface admittance  $M = M_{\text{coh}} + M_{\text{trans}}$  for a Maxwellian and a Lorentzian velocity distribution function, respectively. For the Maxwellian velocity distribution (2.8) we find

$$M_{\text{trans}} = -\frac{2\tilde{K}}{\sqrt{\pi}} \int_0^{\infty} dy y e^{-y^2} \times \left[ \frac{1}{y^2 - \zeta_0^2} + \frac{\eta}{(y + \zeta_0)^2} \right], \quad (3.17)$$

where  $\zeta_0 = i\tilde{\Gamma} - \tilde{\Delta}$ . The coherent part of  $M$  can readily be expressed in terms of the plasma dispersion function  $Z(\zeta_0)$ , cf. (2.22). The integral corresponding to the first term in the square brackets of (3.17) can be expressed in terms of the exponential integral [13]

$$E_1(z) = \int_z^{\infty} \frac{e^{-t}}{t} dt \quad (|\arg z| < \pi). \quad (3.18)$$

The integral corresponding to the second term in the square brackets of (3.17) can be calculated by using

$$y[y + \zeta_0]^{-2} = [y + \zeta_0]^{-1} - \zeta_0[y + \zeta_0]^{-2},$$

partial integration, and the easily verified equality

$$\frac{1}{\sqrt{\pi}} \int_0^{\infty} dy \frac{e^{-y^2}}{y + \zeta_0} = -\frac{1}{2} Z(\zeta_0) + \frac{e^{-\zeta_0^2}}{2\sqrt{\pi}} E_1(-\zeta_0^2). \quad (3.19)$$

In conclusion, from perturbation theory to first order in the optical density  $K$  we deduce that for the case of specular and diffuse wall collisions ( $0 \leq \eta \leq 1$ ) and for a Maxwellian distribution of the velocities of the

vapor atoms, the surface admittance  $M$  is given by the relation

$$\frac{M - 1}{\tilde{K}} = Z(\zeta_0) + \eta \left[ (1 - 2\zeta_0^2) Z(\zeta_0) - 2(1 - \zeta_0^2) \frac{e^{-\zeta_0^2}}{\sqrt{\pi}} E_1(-\zeta_0^2) + \frac{2}{\sqrt{\pi}} - 2\zeta_0 \right] - (1 - \eta) \frac{e^{-\zeta_0^2}}{\sqrt{\pi}} E_1(-\zeta_0^2). \quad (3.20)$$

The first term on the right hand side corresponds to the conventional dispersion theory result (2.22). From the well-known [10, 13] asymptotic expansions of  $Z(\zeta_0)$  and  $E_1(-\zeta_0^2)$  for  $\zeta_0 \rightarrow 0$  and  $\zeta_0 \rightarrow \infty$ , we obtain

$$\frac{M - 1}{\tilde{K}} = i\sqrt{\pi} + \frac{2\eta}{\sqrt{\pi}} \left[ 1 + \gamma_E + \frac{i\pi}{2} + \ln(-\zeta_0^2) \right] + \frac{(1 - \eta)}{\sqrt{\pi}} [\gamma_E + \ln(-\zeta_0^2)] + O(\zeta_0) \quad (\zeta_0 \rightarrow 0) \quad (3.21)$$

and

$$M = 1 - \tilde{K}\zeta_0^{-1} + O(\zeta_0^{-2}) \quad (\zeta_0 \rightarrow \infty), \quad (3.22)$$

where  $\gamma_E = 0.577 21\dots$  is Euler's constant and  $\ln(z)$  is defined for  $|\arg(z)| < \pi$  and  $\ln 1 = 0$ . From (2.14) by expansion with respect to the optical density  $K$  we find to first order in  $K$  that the reflectivity satisfies the relation

$$\frac{\mathbf{R} - \mathbf{R}_0}{\mathbf{R}_0} = -2 \left[ \frac{1}{n_{gl} + 1} + \frac{1}{n_{gl} - 1} \right] \text{Re}[M - 1], \quad (3.23)$$

where the reflectivity  $\mathbf{R}_0$  of the glass is given by

$$\mathbf{R}_0 = \frac{(n_{gl} - 1)^2}{(n_{gl} + 1)^2}. \quad (3.24)$$

From (3.21) and (3.23) one infers that for  $\Gamma < 1$  the reflectivity contains a contribution with a spectral width smaller than the Doppler width. This contribution is logarithmic in nature, is centered at resonance, and, as mentioned before, it is about twice as large for the case of specular wall collisions as it is for the case of diffuse wall collisions. Noting that

$$M_{\text{coh}} = 1 - \tilde{K}\zeta_0^{-1} + O(\zeta_0^{-2})$$

for  $\zeta_0 \rightarrow \infty$ , it is seen from (3.22) that in the far wings of the resonance line ( $|\Delta| \gg 1$ ) and also for  $\Gamma \gg 1$  the surface admittance and the reflectivity are well described by conventional dispersion theory. For the

Lorentzian velocity distribution (2.9) a rather laborious calculation shows that

$$\frac{M - 1}{K} = \frac{i}{1 + \Gamma + i\Delta} + \eta \left\{ \frac{i}{(1 + \Gamma + i\Delta)^2} + \frac{(2/\pi)}{1 - (\Gamma + i\Delta)^2} + \frac{(4/\pi) \ln(\Gamma + i\Delta)}{[1 - (\Gamma + i\Delta)^2]^2} \right\} + (1 - \eta) \frac{(2/\pi) \ln(\Gamma + i\Delta)}{1 - (\Gamma + i\Delta)^2}, \quad (3.25)$$

where the first term on the right hand side corresponds to the conventional dispersion theory result (2.23). For  $\eta = 1$ , i.e. for specular wall collisions, (3.25) is precisely the expression Cojan [3] obtained as the final result of his calculations. It will now be clear that this result is not exact, but a rather special perturbation theory result. In the next section exact calculations of the surface admittance are performed for the case of specular wall collisions. It then turns out that in general Cojan's result, (3.25) with  $\eta = 1$ , is well suited for a comparison with experimentally determined reflectivities even if  $\Gamma$  essentially depends on  $K$ . Finally, it should be noted that for  $\Delta = 0$  the relative reflectivity  $(\mathbf{R} - \mathbf{R}_0)/\mathbf{R}_0$  calculated with the Maxwellian velocity distribution function is about a factor of  $\sqrt{\pi \ln 2}$  larger than the one calculated from the Lorentzian velocity distribution function. This is compatible with the ratios of  $V_M(u)$  and  $V_L(u)$  at zero velocity as discussed in the previous section. Eqs. (3.22) and (3.25) show that in the far wings of the resonance line and for  $\Gamma \gg 1$  the reflectivities calculated with the different velocity distributions differ largely in their behaviour as functions of  $\Delta$  and  $\Gamma$ .

**4. Exact expressions for the case of specular wall collisions.** — To obtain exact expressions for the electric field in the vapor and the surface admittance in the case that we are dealing with specular wall collisions only it is convenient to put formally

$$E(-x) = E(x)$$

and to introduce the dimensionless coordinate  $X = kx$ . Then eqs. (2.5)-(2.7) and (2.10) combine to

$$E''(X) + E(X) + \int_{-\infty}^{\infty} dX' A(X' - X) E(X') = 0, \quad (4.1)$$

where

$$A(X) = 2iK \int_0^{\infty} \frac{dy}{y} V_0(y) \exp \left[ -\frac{|X|}{y} (\Gamma + i\Delta) \right]. \quad (4.2)$$

Primes on  $E$  now denote differentiations with respect to  $X$ . Eq. (4.1) is solved under the assumption that  $E(X)$  is continuous for all  $X$  and absolutely integrable on  $(-\infty, \infty)$ . It follows from (4.1) and (4.2) that  $E'(X)$  and  $E''(X)$  are also absolutely integrable on



( $-\infty, \infty$ ), that  $E''(X)$  is continuous for all  $X$  and that  $E'(X)$  is continuous except at  $X = 0$ . We introduce the Fourier transforms

$$\begin{aligned}\hat{E}(p) &= \int_{-\infty}^{\infty} E(X) e^{-ipX} dX, \\ \hat{A}(p) &= \int_{-\infty}^{\infty} A(X) e^{-ipX} dX.\end{aligned}\quad (4.3)$$

From (4.2) we have

$$\hat{A}(p) = 2iK \int_{-\infty}^{\infty} dy \frac{V_0(y)}{ipy + \Gamma + i\Delta}.\quad (4.4)$$

If  $E'(X)$  tends to  $\alpha$  for  $X \rightarrow +0$ , we find by integrating by parts twice the relation

$$\int_{-\infty}^{\infty} E''(X) e^{-ipX} dX = -p^2 \hat{E}(p) - 2\alpha.\quad (4.5)$$

Thus Fourier transformation of (4.1) results in

$$\hat{E}(p) = \frac{2\alpha}{-p^2 + 1 + \hat{A}(p)}.\quad (4.6)$$

The Fourier inversion formula yields

$$E(X) = \frac{\alpha}{\pi} \int_{-\infty}^{\infty} dp \frac{e^{ipX}}{-p^2 + 1 + \hat{A}(p)}.\quad (4.7)$$

The surface impedance  $M^{-1}$  is related to the electric field at  $X = 0$  by the relation

$$M^{-1} = iE(0)/\alpha.\quad (4.8)$$

The Fourier transform  $\hat{A}(p)$  of the kernel of the integral in (4.1) is discontinuous across the line  $\Gamma p^{(1)} + \Delta p^{(2)} = 0$ , except at  $p = 0$ . Here,  $p^{(1)}$  and  $p^{(2)}$  denote the real part and the imaginary part of  $p$ , respectively. The line of discontinuity is a straight line in the complex  $p$ -plane which passes through  $p = 0$  and makes an angle  $\varphi = \tan^{-1}(-\Gamma/\Delta)$  with the positive real  $p$ -axis. According to whether  $\Gamma p^{(1)} + \Delta p^{(2)}$  is positive or negative we denote  $\hat{A}(p)$  by  $\hat{A}_+(p)$  or  $\hat{A}_-(p)$ , respectively. Across the line of discontinuity, a jump

$$\hat{A}_+(p) - \hat{A}_-(p) = \frac{4\pi iK}{p} V_0\left(\frac{i\Gamma - \Delta}{p}\right)\quad (4.9)$$

occurs in  $\hat{A}(p)$ . On the real  $p$ -axis, however,  $\hat{A}(p)$  is continuous. The zeros of the denominator of the integrand in (4.7) satisfy the relation

$$-p^2 + 1 + \hat{A}(p) = 0.\quad (4.10)$$

Voigt [9] obtained the same implicit relation (2.20) for the complex refractive index  $N$ . As  $\hat{A}(p)$  is an even

function of  $p$  the solutions to (4.10) occur in pairs  $\pm p_1, \pm p_2, \dots$ . At least two solutions exist. To first order in the optical density  $K$  they correspond to

$$p_1 = 1 + \frac{1}{2} \hat{A}(1).\quad (4.11)$$

This equation is the equivalent of (2.21). For the Lorentzian velocity distribution function  $V_L(u)$  it is shown later on in this section that  $p_1$  and  $-p_1$  are the only solutions to (4.10) when  $K \ll 1$ . All the available evidence supports the same conclusion for the Maxwellian velocity distribution  $V_M(u)$ . In the following, it will be assumed that (4.10) has only two solutions,  $p_1$  and  $-p_1$ . The latter solution is not of interest to us as it corresponds to an electric field propagating in the vapor towards the glass-vapor interface. For  $X \geq 0$ , closure of the integral in (4.7) in the upper half plane (UHP) of the complex  $p$ -plane, thereby avoiding crossing the line of discontinuity for  $p \neq 0$ , shows the electric field  $E$  to be the sum of a contribution

$$E_1(X) = \frac{i\alpha}{-p_1 + \frac{1}{2} \frac{d\hat{A}}{dp} \Big|_{p=p_1}} \exp(ip_1 X)\quad (4.12)$$

due to the pole of the integrand at  $p = p_1$  and a contribution

$$\begin{aligned}E_2(X) &= \frac{\alpha}{\pi} \int_C dp \times \\ &\times \frac{[\hat{A}_-(p) - \hat{A}_+(p)] \exp(ipX)}{[-p^2 + 1 + \hat{A}_+(p)] [-p^2 + 1 + \hat{A}_-(p)]}\end{aligned}\quad (4.13)$$

due to the discontinuity of  $\hat{A}(p)$  in the complex  $p$ -plane. The straight integration path  $C$  runs from  $p = 0$  to  $p = \infty \exp(i\varphi)$ . In the conventional dispersion theory the electric field in the vapor is equal to

$$E_{\text{conv}} = -(\alpha/p_1) \exp(ip_1 X).$$

The contribution  $E_1$  is proportional to  $E_{\text{conv}}$  but not equal to it. The electric field in the vapor is not described by a monochromatic wave in the theory presented in this paper but rather by a wave packet with a continuous spectrum. The variation of  $\hat{A}(p)$  with  $p$  shows up in the purely exponential contribution  $E_1(X)$ . Later on in this section it is shown that  $E_2(X)$  is not an exponential contribution to  $E(X)$ . We shall refer to  $E_2$  as the surface excitation. We now first indicate briefly how the perturbation theory result  $M = M_{\text{coh}} + M_{\text{trans}}$  may be rederived from (4.7) and (4.8). Here  $M_{\text{coh}}$  and  $M_{\text{trans}}$  satisfy (3.11) and (3.12), respectively, and  $\eta = 1$ . By introducing a positive infinitely small real number  $\varepsilon$ , rewriting  $-p^2 + 1 + \hat{A}(p)$  in the form

$$\{-p^2 + 1 + 2i\varepsilon\} \{1 + [(\hat{A}(p) - 2i\varepsilon)/(-p^2 + 1 + 2i\varepsilon)]\}$$

and expanding the latter expression with respect to the term in the square brackets to first order in  $K$ , one obtains for the surface admittance  $M$  the following expression :

$$M = 1 - \frac{2K}{\pi} \int_{-\infty}^{\infty} dy V_0(y) \int_{-\infty}^{\infty} \frac{dp}{(p-1-i\epsilon)^2 (p+1+i\epsilon)^2 (ipy + \Gamma + i\Delta)} \quad (4.14)$$

The integral with respect to  $p$  can be evaluated by closure in the UHP and LHP (lower half plane) of the complex  $p$ -plane for  $y < 0$  and  $y > 0$ , respectively. In the limit  $\epsilon \rightarrow 0$ , one obtains from (4.14) the equation

$$M = 1 + 8iK \times \left\{ \frac{d}{dp} \left[ \frac{1}{(p-1)^2} \int_0^{\infty} \frac{dy V_0(y)}{ipy + \Gamma + i\Delta} \right] \right\}_{p=-1} \quad (4.15)$$

and it can easily be shown that the right hand side of this equation equals the above mentioned perturbation theory result of section 3.

Next the surface admittance  $M$  will be evaluated in detail from (4.8), (4.12) and (4.13) for the Lorentzian velocity distribution function  $V_L(u)$ . Numerical calculations are needed for the Maxwellian velocity distribution function  $V_M(u)$ . Such calculations will be reported in the next section using the exact expression for the surface admittance when the wall collisions of the vapor atoms are diffuse instead of specular. This case is the more interesting one for at moderate temperatures wall collisions of atoms are most probably of the diffuse type. If  $V(u) = V_L(u)$ , then  $\hat{A}_+(p)$  and  $\hat{A}_-(p)$  satisfy the relations

$$\hat{A}_{\pm}(p) = \frac{2iK}{\Gamma + i\Delta \pm p} \quad (4.16)$$

The zeros of the equations

$$(\Gamma + i\Delta \pm p)(-p^2 + 1) + 2iK = 0$$

will be denoted by  $\pm p_1$ ,  $\pm p_2$  and  $\pm p_3$ . To first order in the optical density  $K$  we have

$$\left. \begin{aligned} p_1 &= 1 + \frac{iK}{1 + \Gamma + i\Delta}, \\ p_2 &= -1 + \frac{iK}{1 - \Gamma - i\Delta}, \\ p_3 &= -\Gamma - i\Delta - iK \left[ \frac{1}{1 - \Gamma - i\Delta} + \frac{1}{1 + \Gamma + i\Delta} \right]. \end{aligned} \right\} \quad (4.17)$$

It is easily verified that only  $p_1$  satisfies eq. (4.10) as already stated. As none of the zeros  $\pm p_1$ ,  $\pm p_2$  and  $\pm p_3$  is situated in the area in the UHP of the complex  $p$ -plane in between the integration path  $C$

and the positive imaginary  $p$ -axis, one immediately deduces from (4.13) that

$$E_2(X) = -\frac{4i\alpha K}{\pi} \int_0^{i\infty} \times \frac{p \exp(ipX) dp}{(p^2 - p_1^2)(p^2 - p_2^2)(p^2 - p_3^2)} \quad (4.18)$$

It is now straightforward to obtain the following exact expression

$$M^{-1} = \left[ p_1 + \frac{iK}{(\Gamma + i\Delta + p_1)^2} \right]^{-1} - \frac{4K}{\pi} \left[ \frac{\ln(p_1)}{(p_1^2 - p_2^2)(p_1^2 - p_3^2)} + \frac{\ln(-p_2)}{(p_2^2 - p_1^2)(p_2^2 - p_3^2)} + \frac{\ln(-p_3)}{(p_3^2 - p_1^2)(p_3^2 - p_2^2)} \right] \quad (4.19)$$

To first order in the optical density  $K$ , expression (4.19) boils down to

$$M = 1 + \frac{iK}{1 + \Gamma + i\Delta} + \frac{iK}{[1 + \Gamma + i\Delta]^2} + \frac{2K}{\pi} \left[ \frac{1}{1 - (\Gamma + i\Delta)^2} + \frac{2}{[1 - (\Gamma + i\Delta)^2]^2} \ln(-p_3) \right] \quad (4.20)$$

This result deviates from the perturbation theory expression (3.25) with  $\eta = 1$ . For  $\Gamma \ll 1$ , assuming (3.23) to hold, the position of the maximum of the logarithmic contribution to the reflectivity is shifted from  $\Delta = 0$  in (3.25) to  $\Delta \approx -2K$  in (4.20). As the spectral width of the logarithmic contribution is of the order of  $\Gamma$ , the range of validity of (3.25) with  $\eta = 1$  is determined by the condition  $K \ll \Gamma$ , which is precisely the basic assumption of the perturbation theory as developed in the previous section. The range of validity of the perturbation theory result (3.25) with  $\eta = 1$  can be extended to all values of  $K \ll 1$  and  $\Gamma \ll 1$  by replacing  $\Delta$  in the logarithmic contribution to (3.25) by  $\Delta + 2K(1 + \Delta^2)^{-1}$ . Therefore, as already noted, Cojan's [3] expression for the surface admittance which is the same as (3.25) with  $\eta = 1$ , is well suited to make a comparison of theoretical and experimental results for the reflectivity if only relative and not absolute frequencies are compared. For  $\Gamma \gg 1$ , the surface admittance  $M$  as described by (4.20) reduces to the conventional dispersion theory result (2.23), where  $M$  should be identified with  $N$ .

This section is concluded with a discussion of the behaviour of the electric field in the vapor at large distances from the interface. For  $X \rightarrow \infty$ , the surface excitation  $E_2(X)$  as given by (4.13) is mainly determined by values of  $p$  close to zero. As

$$i\Gamma - \Delta = |i\Gamma - \Delta| \exp(i\varphi),$$

on the integration path C we have

$$p = (i\Gamma - \Delta) |i\Gamma - \Delta|^{-1} |p|.$$

Define  $t = |p| / |i\Gamma - \Delta|$  and

$$g(t) = \left\{ - (i\Gamma - \Delta)^2 t^2 + 1 + \hat{A}_+ [(i\Gamma - \Delta)t] \right\}^{-1} \times \\ \times \left\{ - (i\Gamma - \Delta)^2 t^2 + 1 + \hat{A}_- [(i\Gamma - \Delta)t] \right\}^{-1}.$$

We shall approximate  $g(t)$  by  $g(0)$ . The error  $g(t) - g(0) = t^2 S(t)$  and  $S(t)$  is a bounded function on  $0 \leq t < \infty$ . The maximum value of  $S(t)$  on that interval of  $t$ -values is denoted by  $S_0$ . From (4.9) and (4.13) we obtain now

$$E_2(X) = -4iK\alpha \times \\ + \left[ g(0) \int_0^\infty \frac{dt}{t} V_0\left(\frac{1}{t}\right) e^{-(\Gamma+i\Delta)Xt} + R(X) \right], \quad (4.21)$$

where

$$|R(X)| \leq S_0 \int_0^\infty dt t V_0\left(\frac{1}{t}\right) e^{-\Gamma X t} \quad (4.22)$$

and

$$g(0) = (\Gamma + i\Delta)^2 (\Gamma + i\Delta + 2iK)^{-2}. \quad (4.23)$$

For the Lorentzian velocity distribution  $V_L(u)$  it follows by partial integration from (4.21) and (4.22) that

$$E_2(X) = -\frac{4iK\alpha}{\pi} \times \\ \times \left\{ \frac{g(0)}{[(\Gamma + i\Delta)X]^2} + O(X^{-4}) \right\} (X \rightarrow \infty). \quad (4.24)$$

This result has been derived previously by Cojan [3]. For the Maxwellian velocity distribution function  $V_M(u)$  the calculation of the asymptotic behaviour of  $E_2(X)$  as  $X \rightarrow \infty$  is much more involved. Using the saddle point method [14] it is shown in Appendix A that

$$E_2(X) \sim -\frac{4i\tilde{K}\alpha}{\sqrt{3}} g(0) \left[ \frac{2}{(\tilde{\Gamma} + i\tilde{\Delta})X} \right]^{1/3} \times \\ \times \exp \left\{ -3 \left[ \frac{(\tilde{\Gamma} + i\tilde{\Delta})X}{2} \right]^{2/3} \right\} (X \rightarrow \infty). \quad (4.25)$$

The asymptotic behaviour of the surface excitation at large distances from the glass-vapor interface thus depends essentially on the type of velocity distribution function involved. In particular it depends on the behaviour of the velocity distribution function at

large velocities. Mathematically, this is clear from (4.21) as mainly small values of  $t$  contribute to the integral representation of  $E_2(X)$ . Physically, it is also quite understandable. The surface excitation  $E_2(X)$  corresponds to the previously discussed transient polarization behaviour of atoms running towards the interior of the vapor. Therefore, only fast atoms contribute to  $E_2(X)$  at large distances from the interface and as  $X \rightarrow \infty$  the contribution  $E_2(X)$  to the electric field  $E(X)$  in the vapor will be of smaller magnitude for the Maxwellian velocity distribution function than for the Lorentzian velocity distribution function. A comparison of the magnitudes of  $E_1(X)$  and  $E_2(X)$  shows that in general  $|E_2(X)|$  outgrows  $|E_1(X)|$  only at distances from the interface much larger than the absorption length  $l_{\text{abs}}(\omega_0)$ . In conclusion, the theory presented in this section leads to substantial deviations from the conventional results for the reflectivity but has no practical consequences for measurements of the absorption length.

**5. Exact expressions for the case of diffuse wall collisions.** — For diffuse wall collisions of vapor atoms, according to (2.5)-(2.7) and (2.10) the electric field  $E(X)$  in the vapor satisfies the relation

$$E''(X) + E(X) + \int_0^\infty dX' A(X - X') E(X') = 0, \quad (5.1)$$

where  $A(X)$  is given by (4.2). We want to solve this differential-integral equation by means of a Wiener-Hopf technique [7]. For that purpose the Fourier transform  $\hat{A}(p)$  must be regular in a strip  $|p^{(2)}| < q$ . As we have seen in the previous section  $\hat{A}(p)$  does not satisfy such a requirement. However, at this stage it should be realized that the velocity of light  $c$  is the largest possible velocity. If the velocity distribution function  $V(u)$  vanishes for  $|u| > c$  then the line of discontinuity breaks up into two parts with a finite separation in the complex  $p$ -plane and  $\hat{A}(p)$  is regular in the strip  $|p^{(2)}| < q_0$ , where  $q_0 = \bar{u}\Gamma/c = \gamma/\omega$ . Such a result is also obvious from the asymptotic behaviour of the modified kernel

$$A_c(X) = 2iK \int_0^{c/\bar{u}} \frac{dy}{y} V_0(y) \exp \left[ -\frac{|X|}{y} (\Gamma + i\Delta) \right], \quad (5.2)$$

which is given by

$$A_c(X) = O \left[ K \left( \frac{\gamma |X|}{\omega} \right)^{-1} \times \right. \\ \left. \times \exp \left( -\frac{\gamma |X|}{\omega} \right) \right] (|X| \rightarrow \infty). \quad (5.3)$$

The derivation of (5.3) is straightforward once the change of integration variable  $z = c/(\bar{u}y)$  has been performed in (5.2). With the modified kernel (5.2)

Wiener-Hopf techniques can be applied to (5.1). The limit  $c \rightarrow \infty$  is taken afterwards. As the calculations are rather intricate they are presented in Appendix B. Only the final result for the surface admittance is quoted here :

$$M = i + \frac{i}{2\pi} \int_{-\infty}^{\infty} dp \ln \left[ \frac{p^2 - 1 - \hat{A}(p)}{p^2 + 1} \right]. \quad (5.4)$$

We first show that the perturbation theory result  $M = M_{\text{coh}} + M_{\text{trans}}$  can be rederived from (5.4). Here  $M_{\text{coh}}$  and  $M_{\text{trans}}$  satisfy (3.11) and (3.12), respectively, and  $\eta = 0$ . Introducing a positive infinitely small real number  $\varepsilon$ , we write

$$\ln \left[ \frac{p^2 - 1 - \hat{A}(p)}{p^2 + 1} \right] = \ln \left[ \frac{p^2 - 1 - 2i\varepsilon}{p^2 + 1} \right] + \ln \left[ 1 - \frac{\hat{A}(p) - 2i\varepsilon}{p^2 - 1 - 2i\varepsilon} \right]. \quad (5.5)$$

The first term on the right hand side of this equation yields a contribution to (5.4) which equals  $1 - i$ . Expansion of the second term on the right hand side of (5.5) to first order in  $K$  then yields

$$M = 1 + \frac{2K}{\pi} \int_0^{\infty} V_0(y) dy \times \int_{-\infty}^{\infty} \frac{dp}{(p - 1 - i\varepsilon)(p + 1 + i\varepsilon)(ipy + \Gamma + i\Delta)}. \quad (5.6)$$

Further evaluation of this expression runs similar to the evaluation of (4.14). In the limit  $\varepsilon \rightarrow 0$ , the final result is given by

$$M = 1 + 2iK \int_0^{\infty} dy \frac{V_0(y)}{\Gamma + i\Delta - iy}, \quad (5.7)$$

which reproduces the perturbation theory result of section 3 for  $\eta = 0$ .

Next, the surface admittance will be further evaluated from (5.4) for the Lorentzian velocity distribution function  $V_L(u)$ . For that distribution function,  $M$  can be written in the form

$$M = i + \frac{i}{\pi} \int_0^{\infty} \ln \left[ \frac{(p - p_1)(p - p_2)(p - p_3)}{(p - i)(p + i)(p + \Gamma + i\Delta)} \right] dp, \quad (5.8)$$

where  $p_1, p_2$  and  $p_3$  are the zeros of

$$(\Gamma + i\Delta + p)(-p^2 + 1) + 2iK = 0.$$

To first order in the optical density these zeros are given by (4.17). A straightforward calculation of the integral in (5.8) results in

$$M = p_1 + \frac{i}{\pi} [p_1 \ln(p_1) + p_2 \ln(-p_2) + p_3 \ln(-p_3) + (\Gamma + i\Delta) \ln(\Gamma + i\Delta)]. \quad (5.9)$$

Expansion of this expression to first order in  $K$  yields

$$M = 1 + \frac{iK}{1 + \Gamma + i\Delta} + \frac{i}{\pi} \left[ \frac{2iK}{\pi} \frac{1}{1 - (\Gamma + i\Delta)^2} + p_3 \ln(-p_3) + (\Gamma + i\Delta) \ln(\Gamma + i\Delta) \right], \quad (5.10)$$

where  $p_3$  is given by (4.17).

Assuming that the reflectivity is given by relation (3.23), implying it to be proportional to  $\text{Re } M$ , we discuss the difference between the reflectivities  $\mathbf{R}_E$  and  $\mathbf{R}_P$  calculated according to (5.10) and the perturbation theory expression (3.25) with  $\eta = 0$ , respectively. For  $\Gamma \gg 1$ , the difference is negligible. For  $\Gamma \ll 1$ , the main difference shows up in the value of the dimensionless frequency  $\Delta_0$  where the reflectivity is maximum. From (3.25) with  $\eta = 0$  one obtains  $\Delta_0 \approx 0$ , whereas from (5.10) the value  $\Delta_0 \approx -K$  is obtained. Note that for the case of specular wall collisions one obtains  $\Delta_0 \approx -2K$  from (4.20). The maximum values of  $\mathbf{R}_E$  and  $\mathbf{R}_P$ , as well as their values for  $|\Delta| \gg 1$ , do not differ significantly. Therefore, the conclusion is that for diffuse wall collisions and a Lorentzian velocity distribution function the reflectivity  $\mathbf{R}_P$ , calculated from (3.23) and (3.25) with  $\eta = 0$ , for all  $K \ll 1$  and  $\Gamma \ll 1$  is useful for making comparisons between theoretical and experimental results as long as a comparison of absolute frequencies is left out of consideration. For specular wall collisions a similar conclusion was drawn in the previous section.

In an atomic vapor at moderate temperatures it is most probable that the atomic velocities are distributed Maxwellian and that the wall collisions of the vapor atoms are of the diffuse type. Especially for this situation one would like to know the behaviour of the exact expression (5.4) for the surface admittance as a function of  $K, \Gamma$  and  $\Delta$ . In particular, the question arises as to whether the conclusion drawn earlier for the Lorentzian distribution of the atomic velocities, namely that perturbation theory in a sense can be useful for making comparisons between theoretical and experimental results for all  $K \ll 1$  and  $\Gamma \ll 1$ , also holds for a Maxwellian distribution and diffuse wall collisions. We again assume that the reflectivity  $\mathbf{R}$  is given by (3.23), i.e.  $\mathbf{R}$  depends on  $\text{Re } M$  only. Let  $A_1 = \text{Re } \hat{A}$  and  $A_2 = \text{Im } \hat{A}$  ( $A_2 \geq 0$ ) and let  $p_0$  satisfy  $p_0^2 - 1 - A_1(p_0) = 0$ . The numerator

$$p^2 - 1 - \hat{A}(p)$$

of the argument of the logarithm in (5.4) can be written in the form

$$[(p^2 - 1 - A_1)^2 + A_2^2]^{1/2} \exp(i\psi),$$

where

$$\psi = -\pi + \tan^{-1}(-A_2/(p^2 - 1 - A_1))$$

if  $0 \leq p < p_0$ ,  $\psi = \tan^{-1}(-A_2/(p^2 - 1 - A_1))$  if  $p_0 < p < \infty$  and  $\tan^{-1}(z)$  varies between  $-\pi/2$  if  $z = -\infty$  and  $\pi/2$  if  $z = \infty$ . As

$$\text{Re } M = -\pi^{-1} \int_0^\infty \psi(p) dp,$$

we find

$$\text{Re } M = p_0 - \frac{1}{\pi} \int_0^\infty \tan^{-1} \left[ \frac{A_2(p)}{1 + A_1(p) - p^2} \right] dp. \quad (5.11)$$

Note that the integrand is discontinuous at  $p = p_0$ . To first order in the optical density,

$$p_0 = 1 + \frac{1}{2} A_1(1) = \text{Re } p_1,$$

where  $p_1$  is given by (4.11). Therefore the first term on the right hand side of (5.11) corresponds to the expression one obtains for the real part of the surface admittance from conventional dispersion theory, cf. (2.21). For the Maxwellian velocity distribution function  $V_M(u)$  we have

$$\begin{aligned} A_1(p) &= \frac{2\tilde{K}}{p} \text{Re } Z \left( \frac{i\tilde{\Gamma} - \tilde{\Delta}}{p} \right), \\ A_2(p) &= \frac{2\tilde{K}}{p} \text{Im } Z \left( \frac{i\tilde{\Gamma} - \tilde{\Delta}}{p} \right), \end{aligned} \quad (5.12)$$

where  $Z(\zeta)$  is the plasma dispersion function as introduced in section 2. The exact reflectivity  $R_E$  was calculated numerically from (3.23), (5.11) and (5.12). From (3.20) with  $\eta = 0$  and (3.23), the perturbation theory result for the reflectivity  $R_P$  was also calculated numerically. A typical result of these calculations is shown in figure 1, where the reflectivities  $R_E$  and  $R_P$  are plotted as functions of the detuning  $\Delta\nu = \nu - \nu_0$  for  $\Gamma = 0.154$ ,  $K = 0.063$  and  $\Delta\nu_D = 1952$  MHz. The absolute reflectivity scale was obtained assuming a refractive index of the glass of 1.6277. For the values of  $\Gamma$  and  $K$  chosen in figure 1, mean free path and absorption length at the center of the resonance line are about equal and perturbation theory in general is a poor approximation to calculate the reflectivity. Indeed figure 1 shows that  $R_E$  and  $R_P$  have quite different values for  $\Delta \approx 0$ . However, the values of  $R_E$  and  $R_P$  can be brought into close agreement if the center of the spectrum associated with the reflectivity  $R_P$  is shifted over about 60 MHz towards higher

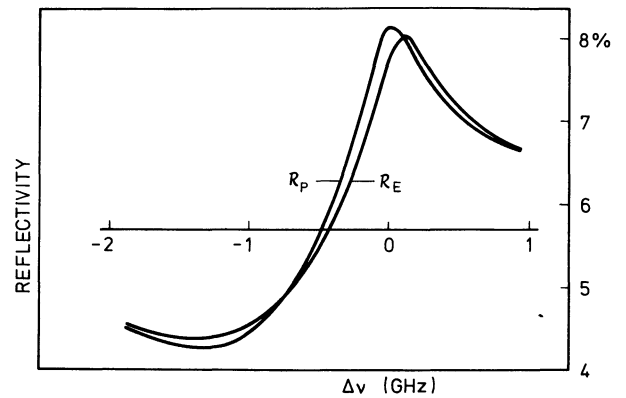


FIG. 1. — Reflectivity  $R$  of a glass-vapor interface versus  $\Delta\nu = \nu - \nu_0$  as calculated from the exact theory ( $R_E$ ) and the low density perturbation theory ( $R_P$ ) for the case of diffuse wall collisions and a Maxwellian distribution of atomic velocities. The natural width  $\Delta\nu_N$ , the collisional width  $\Delta\nu_C$ , the Doppler width  $\Delta\nu_D$ , the optical density  $K$  and the refractive index of the glass  $n_g$  have been taken equal to 10 MHz, 290.6 MHz, 1952 MHz, 0.063 and 1.6277, respectively. The low density formula (3.23) was used to calculate the reflectivity.

frequencies. For  $|\Delta| \gg 1$ ,  $R_E$  and  $R_P$  differ only slightly. Similar results have been obtained for other values of  $\Gamma \ll 1$  and  $K \ll 1$ . In conclusion one can say that the difference between the perturbation theory results of section 3 for  $\eta = 0$  and the exact results of this section is only marginal. For all  $K \ll 1$  and  $\Gamma \ll 1$  the perturbation theory results are quite satisfactory for making comparisons between theoretical and experimental results if comparisons of absolute frequencies are left out of consideration. In the illustrations of the theory that follow we restrict ourselves to the perturbation theory results of section 3.

#### 6. Application to the sodium $D_2$ -resonance line. —

In this section the results obtained are illustrated for the sodium  $D_2$ -resonance line. This line corresponds to a  $3^2S_{1/2} \rightarrow 3^2P_{3/2}$  transition with a wavelength of 5889.95 Å, an oscillator strength  $f$  of 0.655 ( $\pm 3\%$ ) [15] and a natural line width of 10 MHz [8, 15]. Watanabe [16] has calculated the collisional broadening  $\Delta\nu_C$  for the  $D_1$ - and  $D_2$ -lines of sodium, using absorption coefficient data obtained in the far wings of the lines and vapor pressure data as measured by Thiele [17]. He found for the  $D_2$ -line that

$$\Delta\nu_C = 0.8 \times 10^{-13} \times \rho \text{ MHz}$$

where  $\rho$  is given in  $\text{cm}^{-3}$  [18]. Using more recent vapor pressure data [19] figure 2 is obtained for the sodium density as a function of the condensed sodium temperature. From a re-examination of the data in table I of Watanabe's paper using figure 2 one finds for the  $D_2$ -line

$$\Delta\nu_C = (0.70 \pm 0.14) \times 10^{-13} \times \rho \text{ (MHz)}. \quad (6.1)$$

Carrington *et al.* [20] have numerically calculated  $\Delta\nu_C$  for a transition from a  $j = \frac{1}{2}$  ground state to a  $j = \frac{3}{2}$

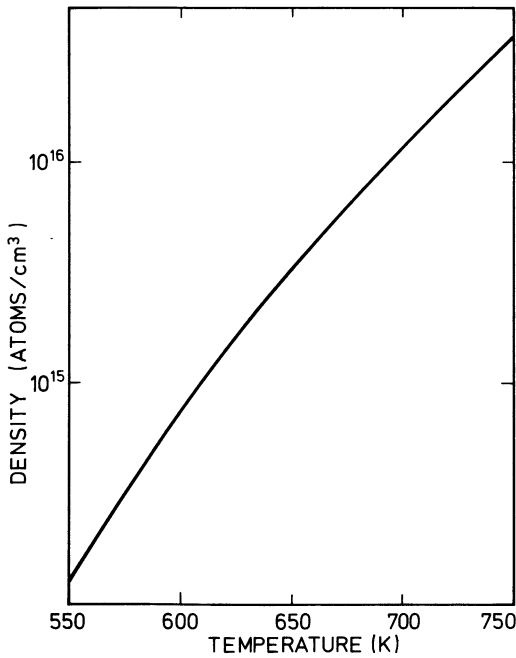


FIG. 2. — Sodium vapor density versus condensed sodium temperature (see ref. [19]).

excited state using the impact approximation and ascribing the width to resonance collisions. Their result is in good agreement with (6.1). The Doppler width can be calculated from the relation

$$\Delta\nu_D = 76.0 \times T^{1/2} \text{ (MHz)}, \quad (6.2)$$

where  $T$  is the absolute temperature of the vapor. From (2.24) one can verify that the optical density  $K$  is given by

$$K = 0.5187 \times 10^{-13} \times \rho \Delta\nu_D^{-1}, \quad (6.3)$$

where  $\rho$  and  $\Delta\nu_D$  are given in  $\text{cm}^{-3}$  and MHz, respectively.

The energy scheme of the sodium  $D_2$ -resonance line is given in figure 3 [21]. The hyperfine structure of the  $3^2P_{3/2}$  state will be neglected in the following. The occupation numbers of the  $F = 1$  and  $F = 2$  ground states are  $\frac{3}{8}$  and  $\frac{5}{8}$ , respectively. Thus, the surface admittance  $M_{D_2}$  corresponding to the  $D_2$ -line is given by the relation

$$M_{D_2} = \frac{5}{8} M(\Delta; K, \Gamma) + \frac{3}{8} M(\Delta + \Delta_S; K, \Gamma), \quad (6.4)$$

where

$$\Delta = 2[\nu(3^2S_{1/2}, F = 2 \rightarrow 3^2P_{3/2}) - \nu]/\Delta\nu_D,$$

$$\Delta_S = 2 \nu_S/\Delta\nu_D$$

and

$$\nu_S = \nu(3^2S_{1/2}, F = 1 \rightarrow 3^2P_{3/2}) - \nu(3^2S_{1/2}, F = 2 \rightarrow 3^2P_{3/2}).$$

For the conventional dispersion theory,  $M(\Delta; K, \Gamma)$  is the complex index of refraction as given by (2.22) and (2.23). For the present theory,  $M(\Delta; K, \Gamma)$  is the surface admittance as given by (3.20) and (3.25). As is obvious from figure 3, the transitions  $F = 2 \rightarrow 3$  and  $F = 1 \rightarrow 1, 2$  are the strongest ones and therefore  $\nu_S$  will be chosen somewhat smaller than the ground state splitting 1772 MHz, namely 1720 MHz. The reflectivity can now be calculated either from the complete Fresnel formula (2.14) or from its low density version (3.23). The only selective reflection experiments on sodium vapor published so far are those of Woerdman [5]. In these experiments the reflection cell is made of gehlenite glass which has a refractive index of 1.6277 at 300 K. This value will be used for  $n_{gl}$ .

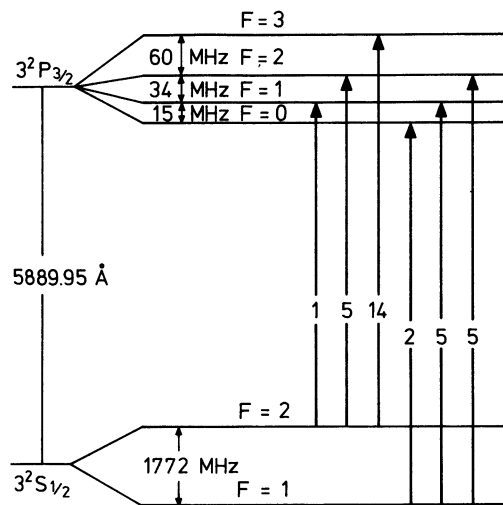


FIG. 3. — Hyperfine structure of the sodium  $D_2$ -resonance line. The ratio of the line strengths is indicated.

In figures 4 and 5 the reflectivity calculated using (6.1)-(6.4) and (3.23) is plotted as a function of  $\Delta\nu = \nu - \nu(3^2S_{1/2}, F = 2 \rightarrow 3^2P_{3/2})$  for the condensed sodium temperatures 610 K and 659 K. In the spectra calculated from the conventional dispersion theory, denoted by NC, the hyperfine splitting of the  $3^2S_{1/2}$  ground state shows up only as a small kink near the center of the spectra. Using the theory given in this paper, including either diffuse wall collisions (DC) or specular wall collisions (SC), a separation into two peaks occurs. The spectra calculated using a Maxwellian or a Lorentzian velocity distribution differ mainly in amplitude (see also section 3). For low enough densities the low frequency peak will be the highest in amplitude according to (6.4). This is the case in the 610 K spectrum, but not in the 659 K spectrum. For only specular wall collisions (SC) the peaks are higher in amplitude than for only diffuse wall collisions (DC). The reflectivity between the peaks is larger than  $R_0$  ( $\approx 5.7\%$ ) in the DC spectra and smaller than  $R_0$  in the SC spectra. We mention that the spectra plotted in figures 4

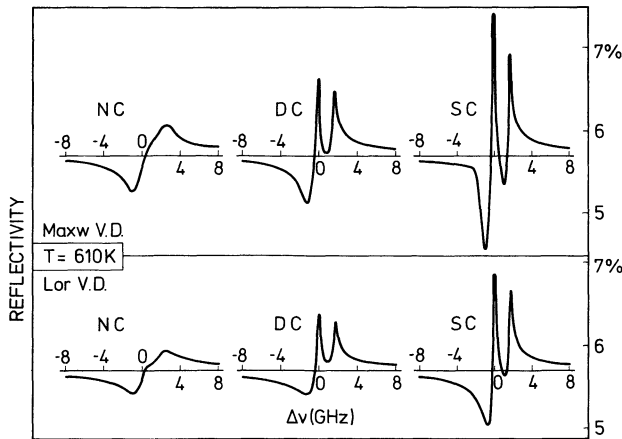


FIG. 4. — Reflectivity of a gehlenite glass-sodium vapor interface near the  $D_2$ -line as calculated for a condensed sodium temperature of 610 K from the low density perturbation results of the conventional theory NC (no wall collisions), the theory for diffuse wall collisions, DC, and the theory for specular wall collisions, SC. The detuning  $\Delta v = \nu - \nu(3^2S_{1/2}, F=2 \rightarrow 3^2P_{3/2})$ . The spectra in the upper half of the figure were calculated from a Maxwellian velocity distribution function, whereas for the calculation of the ones in the lower half of the figure a Lorentzian velocity distribution function was used. All spectra were calculated from the low density formula (3.23) for the reflectivity.

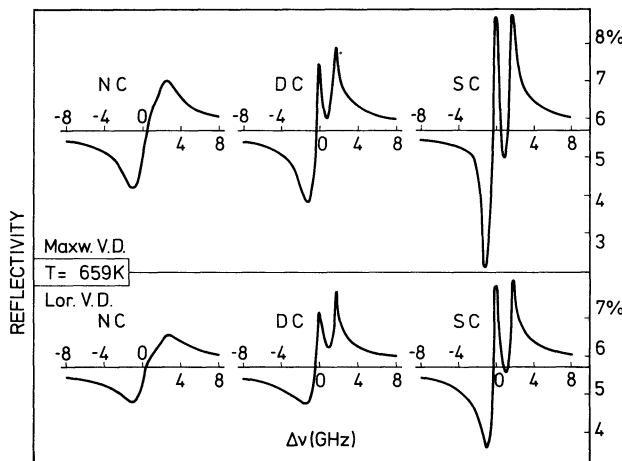


FIG. 5. — Reflectivity of a gehlenite glass-sodium vapor interface near the  $D_2$ -line as calculated for a condensed sodium temperature of 659 K from the low density perturbation results of the conventional theory, NC (no wall collisions), the theory for diffuse wall collisions, DC, and the theory for specular wall collisions, SC. The detuning  $\Delta v = \nu - \nu(3^2S_{1/2}, F=2 \rightarrow 3^2P_{3/2})$ . The spectra in the upper half of the figure were calculated from a Maxwellian velocity distribution function, whereas for the calculation of the ones in the lower half of the figure a Lorentzian velocity distribution function was used. All spectra were calculated from the low density formula (3.23) for the reflectivity.

and 5 do not essentially change if the complete Fresnel formula (2.14) is used.

We shall now indicate some means to test the validity of the present theory. Experimentally one can determine the overall amplitude

$$A = \frac{R_{\max} - R_{\min}}{R_0} \quad (6.5)$$

and the full width at half maximum  $\Delta v(F)$  of the peaks in  $R - R_0$  corresponding to the  $F=1$  and  $F=2$  components of the  $3^2S_{1/2}$  ground state. For given values of  $\Gamma$  and  $K$  the quantities  $A$ ,  $\Delta v(F=1)/\Delta v_D$  and  $\Delta v(F=2)/\Delta v_D$  were calculated numerically for the case of diffuse wall collisions. The overall amplitude  $A$  was also calculated from the conventional dispersion theory. A Maxwellian velocity distribution was assumed in these calculations. From a comparison of the spectra calculated from the complete Fresnel formula and from its small  $K$  version (3.23) it turns out that the reduced amplitude  $A/K$  and the width  $\Delta v(F=2)/\Delta v_D$  as calculated from (2.14) are independent of  $K$  to within a few percents for  $K \lesssim 0.2$ . From best fits to the numerical results of the calculations one obtains for  $K \lesssim 0.2$  the relations

$$(A/K)_{\text{NC}} = 5[1 - 0.004 \ln^3(100\Gamma)] \quad (0.01 < \Gamma < 0.4), \quad (6.6)$$

$$(A/K)_{\text{DC}} = 12.5[1 - 0.167 \ln(100\Gamma)] \quad (0.01 < \Gamma < 0.4), \quad (6.7)$$

$$\Delta v(F=2)/\Delta v_D = 0.095[1 + 1.55\Gamma] \quad (0.01 < \Gamma < 0.3). \quad (6.8)$$

The deviations from the exact numerical results are at the most 5% for (6.6) and (6.7) and 10% for (6.8). According to the conventional dispersion theory  $A/K$  varies only slightly as a function of  $\Gamma$  while in the theory presented in this paper for diffuse wall collisions  $A/K$  varies by a factor of about two going from  $\Gamma = 0.3$  to  $\Gamma = 0.01$ . Eliminating  $\Gamma$  from (6.6) and (6.8) a relation can be obtained between  $A/K$  and  $\Delta v(F=2)/\Delta v_D$ . Since  $\Delta v_C$  and therefore  $\Gamma$  is poorly known, this relation may be most useful in order to test the theory. The value of  $\Gamma$  for which the two peaks are of equal height turns out to be about 0.06. As it is essential for the present theory that, at least for  $K \ll \Gamma$ , the peak maxima occur at the transition frequencies

$$\nu(3^2S_{1/2}, F=1 \rightarrow 3^2P_{3/2})$$

and

$$\nu(3^2S_{1/2}, F=2 \rightarrow 3^2P_{3/2})$$

a frequency calibration could provide another test of the theory.

A first investigation of spectral narrowing in the selective reflection from sodium vapor has been made by Woerdman [5]. A comparison of the experimentally obtained spectra with the theoretical ones obtained from (2.14) and (6.1)-(6.4), assuming diffuse wall collisions and a Maxwellian distribution of the atomic velocities, shows that there is a good qualitative agreement as regards the shape of the spectra. The experimentally determined amplitude  $A$ , however, is smaller by a factor of about two as compared to the amplitude predicted by theory, while the experimental widths of the peaks are larger than the calculated values. In the theoretical spectra equal peak heights

occur at  $\Gamma = 0.06$  corresponding to a condensed sodium temperature of about 620 K. However, experimentally it is found that for  $T = 619$  K the high frequency peak maximum is still larger than the low frequency one. These differences between the experimental and theoretical results cannot be explained by assuming a value of  $\Delta\nu_c$  larger than the one obtained from (6.1). Recently, Burgmans and Woerdman [6] have continued the experimental work on selective reflection from sodium vapor with special emphasis on a quantitative determination of the spectra. A preliminary result of their work is that the amplitudes of the spectra are found to be larger by a factor of about two than those given in figure 2 of reference 5. Experimental and theoretical amplitudes are now no longer inconsistent.

*Note added in proof.* — In a pressure regime where selective reflection is negligible Dodsworth *et al.* [22] have studied wall collisions of atoms in connection with the self-broadening of Hanle signals in back-scattered light.

**Acknowledgments.** — It is a pleasure to thank Pr. D. Polder and Dr. J. P. Woerdman for stimulating and helpful discussions.

**Appendix A.** — Asymptotic expressions for  $\text{Re } a \rightarrow \infty$  will be derived for the integrals

$$I_1 = \frac{1}{\sqrt{\pi}} \int_0^\infty \frac{dt}{t} e^{-t^{-2}} e^{-at}, \quad (\text{A.1})$$

and

$$I_2 = \frac{1}{\sqrt{\pi}} \int_0^\infty dt t e^{-t^{-2}} e^{-at}. \quad (\text{A.2})$$

To calculate the asymptotics of  $I_1$ , we transform to the integration variable  $s = \ln t$  to get

$$I_1 = \frac{1}{\sqrt{\pi}} \int_{-\infty}^\infty ds e^{h(s)}, \quad h(s) = -e^{-2s} - a e^s \quad (\text{A.3})$$

and then follow Laplace's method [14]. The position  $s_0$  of the saddle point of  $h(s)$  satisfies the relation

$$\exp(3 s_0) = (2/a)$$

and in the vicinity of  $s_0$ ,

$$h(s) = h(s_0) + \frac{1}{2}(s - s_0)^2 h''(s_0),$$

where

$$h(s_0) = -3(a/2)^{2/3}$$

and

$$h''(s_0) = 2 h(s_0).$$

One finally obtains

$$I_1 \sim \left[ -\frac{1}{2} h''(s_0) \right]^{-1/2} e^{h(s_0)} = \frac{1}{3} \sqrt{3} \left( \frac{a}{2} \right)^{-1/3} \times \exp \left[ -3 \left( \frac{a}{2} \right)^{2/3} \right] \quad (\text{Re } a \rightarrow \infty). \quad (\text{A.4})$$

The integral  $I_2$  can be treated in a similar way if we transform to the integration variable  $s = t^2$  :

$$I_2 = \frac{1}{2\sqrt{\pi}} \int_0^\infty ds e^{h(s)}, \quad h(s) = -s^{-1} - a \sqrt{s}. \quad (\text{A.5})$$

The position of the saddle point  $s_0 = (2/a)^{2/3}$  and

$$h(s) = h(s_0) + \frac{1}{2}(s - s_0)^2 h''(s_0),$$

where

$$h(s_0) = -3(a/2)^{2/3}$$

and  $h''(s_0) = -\frac{3}{8} a^2$ . Therefore

$$I_2 \sim \frac{2}{3} \sqrt{3} a^{-1} \exp \left[ -3 \left( \frac{a}{2} \right)^{2/3} \right] \quad (\text{Re } a \rightarrow \infty). \quad (\text{A.6})$$

**Appendix B.** — Eq. (5.1) will be solved under the assumption that  $E(X)$  is continuous for  $X > 0$  and bounded for  $X \geq 0$ . It follows from (5.1) that  $E'(X)$  and  $E''(X)$  have the same properties. Where necessary in the following calculations,  $A(X)$  is the modified kernel  $A_c(X)$  as given by (5.2). We extend (5.1) to

$$D(X) = E''(X) + E(X) + \int_{-\infty}^X A(X - X') E(X') dX' \quad (-\infty < X < \infty), \quad (\text{B.1})$$

where  $E(X) = 0$  for  $X < 0$ ,  $D(X) = 0$  for  $X > 0$  and  $D(X)$  is defined by the right hand side of (B.1) for  $X < 0$ . From the asymptotic behaviour (5.3) of  $A(X)$  one deduces  $D(X) = O(\exp[q_0 X])$  as  $X$  tends to  $-\infty$ . Here  $q_0 = \gamma/\omega$ . The Fourier transform of a function  $f(X)$  is defined by

$$\hat{f}(p) = \int_{-\infty}^\infty f(X) e^{-ipX} dX. \quad (\text{B.2})$$

By theorems III and V of Paley and Wiener [23],  $\hat{E}$  and  $\hat{E}''$  are regular for  $p^{(2)} < 0$ ,  $\hat{D}$  is regular for  $p^{(2)} > -q_0$  and  $\hat{A}$  is regular for  $|p^{(2)}| < q_0$ . Moreover,  $\hat{E}$  and  $\hat{E}''$  are bounded for  $p^{(2)} \leq p_0 < 0$ ,  $\hat{D}$  is bounded for  $p^{(2)} \geq p_0 > -q_0$  and  $\hat{A}$  is bounded for  $|p^{(2)}| \leq p_0 < q_0$ . Successive integration by parts shows that

$$\hat{E}''(p) = p^2 \hat{E}(p) - i\beta p - \alpha \quad (p^{(2)} < 0). \quad (\text{B.3})$$



where

$$\alpha = \lim_{x \rightarrow +0} E'(X) \quad \text{and} \quad \beta = \lim_{x \rightarrow +0} E(X).$$

Hence we find

$$\hat{E}(p) = -\frac{i\beta}{p} - \frac{\alpha}{p^2} + O\left(\frac{1}{p^3}\right) \quad (|p| \rightarrow \infty, p^{(2)} \leq p_0 < 0). \quad (\text{B.4})$$

Fourier transformation of (B.1) yields, using (B.3), the equation

$$\hat{D}(p) + i\beta p + \alpha = \hat{E}(p) [-p^2 + 1 + \hat{A}(p)] \quad (-q_0 < p^{(2)} < 0). \quad (\text{B.5})$$

The zeros of  $-p^2 + 1 + \hat{A}(p)$  have been extensively discussed in section 5. It is always possible to find a strip  $|p^{(2)}| \leq q_1 < q_0$  where  $-p^2 + 1 + \hat{A}(p)$  has no zeros. Define a function

$$\tau(p) = \frac{p^2 - 1 - \hat{A}(p)}{p^2 + 1}. \quad (\text{B.6})$$

It is regular and free from zeros in the strip  $|p^{(2)}| \leq q_1$  and

$$\int_{-\infty}^{\infty} |\tau(p^{(1)} + ip^{(2)}) - 1|^2 dp^{(1)} < C(q_2)$$

in each interior strip  $|p^{(2)}| \leq q_2 < q_0$ . Using Cauchy's integral theorem one can now prove (Titchmarsh [24], p. 339) that

$$\tau(p) = \tau_+(p)/\tau_-(p), \quad (\text{B.7})$$

$$\ln \tau_+(p) = -\frac{1}{2\pi i} \int_{iq_3 - \infty}^{iq_3 + \infty} \frac{\ln \tau(p')}{p' - p} dp', \quad (\text{B.8})$$

$$\ln \tau_-(p) = -\frac{1}{2\pi i} \int_{-iq_3 - \infty}^{-iq_3 + \infty} \frac{\ln \tau(p')}{p' - p} dp', \quad (\text{B.9})$$

where  $q_1 < q_3 < q_0$ , but  $q_3 - q_1$  is so small that  $\tau(p)$  has no zero in  $q_1 < |p^{(2)}| \leq q_3$ . Now  $\tau_+(p)$  is regular and free from zeros in  $p^{(2)} \leq q_1$ ,  $\tau_-(p)$  is regular and free from zeros in  $p^{(2)} \geq -q_1$  and in their respective half-planes of regularity  $|\tau_+(p)|$  and  $|\tau_-(p)|$  lie between positive bounds. The functions

$$\Phi_+(p) = (ip + 1) \tau_+(p)$$

and

$$\Phi_-(p) = \tau_-(p)/(ip - 1)$$

satisfy

$$-p^2 + 1 + \hat{A}(p) = \frac{\Phi_+(p)}{\Phi_-(p)} \quad (|p^{(2)}| \leq q_1). \quad (\text{B.10})$$

Using this relation we can write (B.5) in the form

$$\Phi_-(p) [\hat{D}(p) + i\beta p + \alpha] = \hat{E}(p) \Phi_+(p) \quad (|p^{(2)}| \leq q_1). \quad (\text{B.11})$$

The left hand side of this equality is regular for  $p^{(2)} \geq -q_1$ , the right hand side for  $p^{(2)} < 0$ . Thus (B.11) defines an entire function. As  $ip\hat{E}(p) = \beta$  and  $(ip)^{-1} \Phi_+(p) = 1$  in the limit  $|p^{(1)}| \rightarrow \infty$ , we find

$$\hat{E}(p) = \frac{\beta}{\Phi_+(p)} \quad (p^{(2)} \leq q_1), \quad (\text{B.12})$$

and the electric field  $E(X)$  is given by

$$E(X) = \frac{\beta}{2\pi} \int_{-\infty}^{\infty} \frac{e^{ipX}}{\Phi_+(p)} dp. \quad (\text{B.13})$$

It can be shown that (B.13) indeed represents a unique solution of (5.1) using methods similar to those used for the Wiener-Hopf equation [6, 23]. The value of the surface admittance  $M = \alpha/(i\beta)$  is obtained as follows. From (B.4) and (B.12) it is seen that

$$M = \lim_{p^{(1)} \rightarrow \infty} \left[ \frac{ip^2}{\Phi_+(p)} - p \right]. \quad (\text{B.14})$$

According to (B.8) an asymptotic expansion of  $\tau_+(p)$  for  $p^{(1)} \rightarrow \infty$  results in

$$\tau_+(p) = 1 + \frac{\theta}{ip} + O(|p|^{-2}),$$

$$\theta = \frac{1}{2\pi} \int_{-\infty}^{\infty} \ln \tau(p') dp'. \quad (\text{B.15})$$

From this relation and  $\Phi_+(p) = (ip + 1) \tau_+(p)$  one finally obtains

$$M = i(\theta + 1). \quad (\text{B.16})$$

References

[1] WOOD, R. W., *Phil. Mag.* **18** (1909) 187.  
 [2] BORN, M., *Optik* (Springer, Berlin), 1933.  
 [3] COJAN, J. L., *Ann. Phys. (Paris)* **9** (1954) 385.  
 [4] All spectral widths mentioned are full widths at half maximum of the absorption.  
 [5] WOERDMAN, J. P. and SCHUURMANS, M. F. H., *Opt. Commun.* **16** (1975) 248.  
 [6] BURGMANS, A. L. J. and WOERDMAN, J. P., *J. Physique* **37** (1976) juin.  
 [7] HOPF, E., *Mathematical Problems of Radiative Equilibrium* (Cambridge Univ. Press, England) 1934.

- [8] MITCHELL, A. C. G. and ZEMANSKY, M. W., *Resonance Radiation and Excited Atoms* (Cambridge Univ. Press, England) 1934.
- [9] VOIGT, W., *Sitzber. Math. Phys.* (München) (1912) 603.
- [10] FRIED, B. D. and CONTE, S. D., *The Plasma Dispersion Function* (Ac. Press, New York/London) 1961.
- [11] LORENTZ, H. A., *Ann. Phys.* **9** (1880) 641 ;  
LORENZ, L., *Ann. Phys.* **11** (1881) 70.
- [12] WEISSKOPF, V. F., *Z. Phys.* **34** (1933) 1.
- [13] ABRAMOWITZ, M. and STEGUN, I. A., *Handbook of Mathematical Functions* (Nat. Bur. Stand. Appl. Math. Ser. 55, Washington) 1964.
- [14] DE BRUYN, N. G., *Asymptotic Methods in Analysis* (North-Holland Publ. Co., Amsterdam) 1961.
- [15] WISE, W. L., SMITH, M. W. and MILES, B. M., *Atom Transitions Probabilities* (NSRDS-NBS 22, Washington) 1969, Vol. II.
- [16] WATANABE, K., *Phys. Rev.* **59** (1941) 151.
- [17] THIELE, E., *Ann. Phys.* **14** (1932) 937.
- [18] More recently, TOMISER, J., *Acta Phys. Austriaca* **8** (1953) 198 has measured the collisional broadening of the sodium D<sub>2</sub>-line. However, as was noted by CHEN, C. L. and PHELPS, A. V., *Phys. Rev.* **173** (1968) 62 his results are probably erroneous.
- [19] HULTGREN, R., DESAI, P. D., HAWKINS, D. T., GLEISER, M., KELLEY, K. K. and WAGMAN, D. D., *Selected Values of the Thermodynamic Properties of the Elements* (American Society for Metals, Metals Park, Ohio) 1973.
- [20] CARRINGTON, C. G., STACEY, D. N. and COOPER, J., *J. Phys.* **B6** (1973) 417.
- [21] ACKERMAN, H., *Z. Phys.* **194** (1966) 253 ;  
SCHUDA, F., HERCHER, M. and STROUD Jr., C. R., *Appl. Phys. Lett.* **22** (1973) 360.
- [22] DODSWORTH, B. M., GAY, J. C. and OMONT, A., *J. Physique* **33** (1972) 65.
- [23] PALEY, R. E. A. C. and WIENER, N., *Fourier Transforms in the Complex Domain* (American Mathematical Society Colloquium Publications) 1934, Vol. XIX.
- [24] TITCHMARSH, E. C., *Introduction to the Theory of Fourier Integrals* (At the Clarendon Press, Oxford) 1948, 2nd ed.
-