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Edited by

BARRY SALTZMAN

VOLUME 20

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# PREFACE

The rapid growth of geophysical research over the past 25 years has led to an increasing need for syntheses, summaries, and interpretive reductions of the profusion of emerging results. Four examples of such reviews in the area of atmospheric science appear in this volume, covering aspects of the theory of radiation, planetary convection, scaling of dynamic processes, and climate modeling. It is our hope that future volumes will emphasize other areas of interest, in keeping with the role of *Advances in Geophysics* as a forum for reviews of recent progress in understanding all of the geophysical domains ranging from the cores of the celestial bodies to their outer exospheres. It is a pleasure, as the new editor of this serial publication, to invite contributions from scientists in all of the many geophysical disciplines that are embraced by this vast realm. Although such contributions would naturally be mainly of a review nature, this need not preclude the inclusion of substantial new material that can lend a creative and critical aspect to the reduction process and convey a sense of movement in new directions.

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# MODELS FOR INFRARED ATMOSPHERIC RADIATION

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## 1. INTRODUCTION

The study of radiative transmission in real (nonhomogeneous) atmospheres requires a detailed knowledge of the atmospheric constituents that absorb and emit significantly in the spectral range of interest. One of the important quantities required for calculating the atmospheric transmittance is the absorption coefficient of the atmospheric constituents. An accurate model for the spectral absorption coefficient is of vital importance in the correct formulation of the radiative flux equations that are employed for the reduction of data obtained from either direct or remote measurements.

A systematic representation of the absorption by a gas, in the infrared, requires the identification of the major infrared bands and evaluation of the




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line parameters of these bands. The line parameters depend upon the temperature, pressure, and concentration of the absorbing molecules, and, in general, these quantities vary continuously along a nonhomogeneous path through the atmosphere. Even though it is quite difficult to reproduce the real nonhomogeneous atmosphere in the laboratory, considerable efforts have been expended in obtaining the absorption coefficients of important atmospheric constituents. With the availability of high-resolution spectrometers, it is now possible to determine the line positions, intensities, and half-widths of spectral lines quite accurately (McClatchey *et al.*, 1972, 1973; Selby and McClatchey, 1975; Ludwig *et al.*, 1973; Science Application Incorporated, 1973). As a result, absorption by the strong infrared bands of gases like CO, $CO_2$, $N_2O$, $H_2O$, $CH_4$, $NH_3$, and $O_3$ are now known quite well.

In theoretical calculations of transmittance (or absorptance) of a band, a convenient line or band model, for the variation of the spectral absorption coefficient, is used. High spectral resolution measurements make it necessary to employ line-by-line models for transmittance calculations. If, however, the integrated signals are measured over a relatively wide spectral interval, then one could employ an appropriate band model. The line models usually employed in the study of atmospheric radiation are Lorentz, Doppler, and combined Lorentz–Doppler (Voigt) line profiles. A complete formulation (and comparison) of the transmittance (and absorptance) by these lines, in an infinite and a finite spectral interval, is given in Tiwari (1973), Tiwari and Batki (1974), and Tiwari and Reichle (1974). The band models available in the literature are the narrow band models (such as Elsasser, statistical, random-Elsasser, and quasi-random) and the wide band models (such as coffin, modified box, exponential, and axial). The expressions for wide band absorptance are obtained from the general formulations of the narrow band models. In radiative transfer analyses, the use of band models results in a considerable reduction in computational time. Essential information on various narrow band models is available in Elsasser (1942), Plass (1958, 1960), Wyatt *et al.* (1962), Goody (1964a), Kunde (1967), Gupta and Tiwari (1975), and Tiwari and Batki (1975) and on wide band models in Tiwari (1976), Tiwari and Batki (1975), Tien (1968), Cess and Tiwari (1972), and Edwards (1976). The most appropriate model for atmospheric application is the quasi-random narrow band model which is discussed in detail in Wyatt *et al.* (1962), Kunde (1967), and Gupta and Tiwari (1975).

The earth's surface, with its temperature in the vicinity of 300°K, emits like a black body from the near to the far-infrared region of the spectrum. The emission in the infrared range (between 2 and 20 $\mu$m) is particularly important because most of the minor atmospheric constituents (i.e., $CO_2$, $N_2O$, $H_2O$, CO, $CH_4$, $NH_3$, etc.) absorb and emit this spectral region. The upwelling infrared radiation from the earth's atmosphere, therefore, consists of the modulated surface radiation and the radiation from the atmosphere. This radiation carries the spectral signature of all the minor atmospheric constituents, among which gases such as CO, $CH_4$, and $NH_3$ are called the atmospheric pollutants. Ludwig *et al.* (1973) have explored the possibilities of measuring the amount of atmospheric pollutants through remote sensing. An important method of measuring the pollutant concentration by remote sensing is the passive mode (also called the nadir experiment) in which the earth-oriented detector receives the upwelling atmospheric radiation. The near-infrared region is particularly suitable for passive mode measurements simply because the radiation in this region is practically free from the scattering effects. Radiation in the visible and ultraviolet regions is severely affected by the scattering processes which make meaningful passive mode measurements impossible.

The purpose of this study is to review various line and band models and to present analysis procedure for calculating the atmospheric transmittance and upwelling radiance. Various expressions for absorption by different line and band models are presented in Sections 2 and 3. Theoretical formulations of atmospheric transmittance are given in Section 4, where homogeneous path transmittances are calculated for selected infrared bands. The basic equations for calçulating the upwelling atmospheric radiance are presented in Section 5, where model calculations are made to study the effects of different interfering molecules, water vapor profiles, ground temperatures, and ground emittances on the upwelling radiance.

## 2. Absorption by Spectral Lines

In order to describe the infrared absorption characteristics of a radiating molecule it is necessary to consider the variation of the spectral absorption coefficient for a single line. In general, for a single line centered at the wave number $\omega_j$, this is expressed as

$$\kappa_{\omega j} = S_j f_j(\omega, \gamma_j) \tag{2.1}$$

where $S_j$ is the intensity of the $j$th spectral line and is given by

$$S_j = \int_{-\infty}^{\infty} \kappa_{\omega j}\, d(\omega - \omega_j) \tag{2.2}$$

The line intensity may be described in terms of the molecular number density and Einstein coefficients, i.e., it depends upon the transition probabilities between the initial and final states and upon the populations of these states. For a perfect gas it may be shown that $S_j$ is a function solely of temperature. The quantity $f_j(\omega, \gamma_j)$ is the line shape factor for the $j$th spectral line. It is a function of the wave number $\omega$ and the line half-width $\gamma_j$ and is normalized on $\omega - \omega_j$ such that

$$\int_{-\infty}^{\infty} f_j(\omega - \omega_j)\, d(\omega - \omega_j) = 1 \tag{2.3}$$

Several approximate line profiles have been described in the literature. The most commonly used profiles are rectangular, triangular, Lorentz, Doppler, or Voigt (combined Lorentz and Doppler) profiles. The study of line shapes and line broadening is an active research field. For various reviews on the subject, reference should be made to Goody (1964a), Mitchell and Zemansky (1934), Penner (1959), Baranger (1962), Allen (1963), Griem (1964), Cooper (1966), Jefferies (1968), Kondratyev (1969), and Armstrong and Nicholls (1972). Lorentz, Doppler, and Voigt profiles are of special interest in the atmospheric studies, and these are discussed in some detail here.

The line profile usually employed for studies of infrared radiative transfer in the earth's atmosphere is the Lorentz pressure-broadened line shape for which the shape factor is such that the expression for absorption coefficient is found to be

$$\kappa_{\omega j} = S_j f_j(\omega, \gamma_L) = S_j \gamma_L / \{\pi[(\omega - \omega_j)^2 + \gamma_L^2]\} \tag{2.4}$$

where $\gamma_L$ is the Lorentz line half-width. From simple kinetic theory it may be shown that $\gamma_L$ varies with pressure and temperature according to the relation

$$\gamma_L = \gamma_{L0}(P/P_0)^m (T_0/T)^n \tag{2.5}$$

where $\gamma_{L0}$ is the line half-width corresponding to a reference temperature $T_0$ and a pressure $P_0$. The values of $m$ and $n$ depend, in general, on the collision parameters and on the nature of the molecules. A discussion on the variation of $\gamma_L$ with $P$ and $T$ is given in Penner (1959), Yamamoto *et al.* (1969), Ely and McCubbin (1970), and Tubbs and Williams (1972). The value of $m = 1$ and $n = 0.5$ is usually employed for most atmospheric studies.

The maximum absorption coefficient occurs at $\omega = \omega_j$ and is given by the expression

$$(\kappa_{\omega j})_{\omega = \omega j} = S_j / \pi \gamma_L \tag{2.6}$$

The variation of $\kappa_\omega$ over a specific wave number range containing $n$ independent lines is given by

$$\kappa_\omega = \sum_{j=1}^{n} \kappa_{\omega j} \tag{2.7}$$

For Lorentzian line profiles, Eq. (2.7) can be expressed as

$$\kappa_\omega = \sum_j \kappa_{\omega j} = \sum_j S_j \gamma_{Lj} / \{\pi[(\omega - \omega_j)^2 + \gamma_{Lj}^2]\} \tag{2.8}$$

Note that for the Lorentz line profile, $\gamma_L$ varies linearly with the pressure. Thus, in a spectral interval containing many lines, the discrete line structure will be smeared out at sufficiently high pressure.

For Doppler-broadened lines, the absorption coefficient (Mitchell and Zemansky, 1934; Penner, 1959) is given by the relation

$$\kappa_{\omega j} = S_j f_j(\omega, \gamma_D) \tag{2.9a}$$

where

$$f_j(\omega, \gamma_D) = (1/\gamma_D)(\ln 2/\pi)^{1/2} \exp[-(\omega - \omega_j)^2(\ln 2/\gamma_D^2)]. \tag{2.9b}$$
$$\gamma_D = (\omega_j/c)(2kT \ln 2/m)^{1/2}$$

In this equation $\gamma_D$ represents the Doppler half-width, $c$ is the speed of light, $\kappa$ is the Boltzmann constant, and $m$ is the molecular mass. Doppler broadening is associated with the thermal motion of molecules. From Eqs. (2.9) it is clear that the Doppler width depends not only on temperature but also on molecular mass and the location of the line center. For certain atmospheric conditions, therefore, the Doppler and Lorentz widths may become equally important for a particular molecule radiating at a specific frequency. For comparable intensities and half-widths, however, the Doppler line has more absorption near the center and less in the wings than the Lorentz line (Fig. 1).

For radiative transfer analyses involving gases at low pressures (upper atmospheric conditions), it becomes imperative to incorporate the combined influence of the Lorentz and the Doppler broadening. The shape factor for

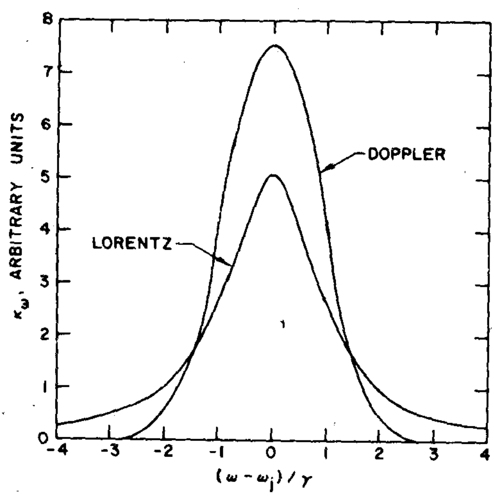


FIG. 1. Comparison of Lorentz and Doppler line profiles having equal line intensities.

the combined profile (Mitchell and Zemansky, 1934; Penner, 1959) is given by

$$\kappa_{\omega j} = S_j f_j(a, v) = \kappa_0 K(a, v) \tag{2.10}$$

where

$$f_j(a, v) = (1/\gamma_D)(\ln 2/\pi)^{1/2} K(a, v)$$

$$K(a, v) = (a/\pi) \int_{-\infty}^{\infty} \{\exp(-t^2)/[a^2 + (v - t)^2]\}\, dt$$

$$\kappa_0 = (S_j/\gamma_D)(\ln 2/\pi)^{1/2} = (S_j/\sqrt{\pi})(a/\gamma_L)$$

$$v = [(\omega - \omega_j)/\gamma_D](\ln 2)^{1/2} = (\omega - \omega_j)(a/\gamma_L)$$

$$a = [(\gamma_c + \gamma_N)/\gamma_D](\ln 2)^{1/2}$$

The function $K(a, v)$ defined in Eq. (2.10) is called the Voigt function, $\gamma_c$ is the collisional broadened half-width, and $\gamma_N$ is the natural line half-width. Usually $\gamma_N$ can be neglected in comparison to $\gamma_c$. At very low pressures (upper atmospheric conditions), however, the contribution from $\gamma_N$ becomes significant. The combined effect of $\gamma_c$ and $\gamma_N$ is frequently represented by $\gamma_L$, and the parameter $a$ is interpreted as the ratio of the Lorentz and Doppler half-widths. As the pressure becomes small, $\gamma_L$ approaches zero and Eq. (2.10) reduces to the absorption coefficient for the Doppler broadened lines which may now be expressed as

$$\kappa_{\omega j} = \kappa_0 \exp(-v^2) \tag{2.11}$$

On the other hand, for large pressures, the quantity $\gamma_L/\gamma_D$ becomes large and Eq. (2.10) reduces to the Lorentzian case, Eq. (2.4). In other words, the Voigt profile assumes the Lorentzian shape in the limit of large $v$ and reduces to the Doppler profile for small $a$. The Voigt function is referred to as the reduced absorption coefficient, with $\kappa_0$ representing its dimensional constant. The origin and properties of the Voigt function and methods of computing it are reviewed in some detail in Armstrong and Nicholls (1972) where it is shown that $K(a, v)$ is the real part of the complex error function.

Several alternate and approximate forms of the Voigt function, and a number of tabulations of these forms, are available in Mitchell and Zemansky (1934), Penner (1959), Armstrong and Nicholls (1972), Reiche (1913), Born (1933), Van de Hulst and Reesinck (1947), Harris (1948), Penner and Kavanagh (1953), Plass and Fivel (1953), Posener (1959), Fried and Conte (1961), Hummer (1964a,b, 1965), Finn and Mugglestone (1965), Young (1965a,b), and Armstrong (1967). With the aid of computer programs developed by Hummer (1964a,b, 1965), Young (1965a,b), Armstrong (1967), Chiarella and Reichel (1968), and Gautschi (1969, 1970), it is now possible to calculate the Voigt function (for an extended range of parameters) to an accuracy of better than six significant figures.

A simple closed form approximation to the Voigt profile that is valid over a useful range of parameters is given, in terms of the present nomenclature (Van de Hulst and Reesinck, 1947; Posener, 1959; Whiting, 1968), by

(2.12a) $$\kappa_{\omega j}/\kappa_{\omega 0} = [1 - (\gamma_L/\gamma_V)] \exp\{-11.088[(\omega - \omega_j)/\gamma_V]^2\} + (\gamma_L/\gamma_V)/\{1 + 16[(\omega - \omega_j)/\gamma_V]^2\}$$

where Voigt half-width is expressed in terms of $\gamma_L$ and $\gamma_D$ as

(2.12b) $$\gamma_V = (\gamma_L/2) + [(\gamma_L^2/4) + \gamma_D^2]^{1/2}$$

and

(2.12c) $$\kappa_{\omega 0} = S_j/\{\gamma_V[1.065 + 0.447(\gamma_L/\gamma_V) + 0.058(\gamma_L/\gamma_V)^2]\}$$

This form is very convenient for numerical computation, and it matches the Voigt profile within 5 % under worst conditions. Generally the error is within 3 %, with maximum errors occurring near zero pressures. A somewhat better approximation for the Voigt function is suggested by Kielkopf (1973).

The radiative transmittance at a single wave number is given by the relation

(2.13) $$\tau_{\omega j} = \exp\left(-\int_0^X \kappa_{\omega j}\, dX\right)$$

where $X = \int_0^\ell \rho_a\, d\ell$ is the mass of the absorbing gas per unit area, $\kappa_{\omega j}$ is the mass absorption coefficient for the $j$th spectral line, $\ell$ is the length measured along the direction of the path which makes an angle $\theta$ with the vertical, and $\rho_a$ is the density of the absorbing gas. For a homogeneous path, Eq. (2.13) becomes

(2.14) $$\tau_{\omega j} = \exp(-\kappa_{\omega j} X)$$

The total absorption of a single line, in an infinite spectral interval, is given by

(2.15) $$A_j = \int_{-\infty}^{\infty} (1 - \tau_{\omega j})\, d(\omega - \omega_j)$$

where $\omega_j$ represents the wave number at the line center of the $j$th spectral line. For a homogeneous path, this can be expressed as

(2.16) $$A_j = \int_{-\infty}^{\infty} [1 - \exp(-\kappa_{\omega j} X)]\, d(\omega - \omega_j)$$

For small values of the quantity $\kappa_{\omega j} X$, Eq. (2.16) reduces to an important limiting form which is independent of any spectral model used for $\kappa_{\omega j}$. This is the conventional optically thin (or linear) limit in radiative transfer. This limit is obtained by expanding the exponential in Eq. (2.16) and retaining only the first two terms in the series such that

$$A_j = X \int_{-\infty}^{\infty} \kappa_{\omega j}\, d(\omega - \omega_j) = X S_j \tag{2.17}$$

Another limit, which does depend upon the particular model employed for $\kappa_{\omega j}$, is the square-root limit or the strong line approximation for which the total absorption occurs in the vicinity of the line center. To find expressions for absorptance in this limit, it is required that $(\kappa_{\omega j} x) \gg 1$ for $\omega = \omega_j$.

The average absorption $\bar{A}$ of a single line, which is a member of a group of lines, is given by

$$\bar{A}_j = \frac{1}{d} \int_{-\infty}^{\infty} [1 - \exp(-\kappa_{\omega j} X)]\, d(\omega - \omega_j) \tag{2.18}$$

where $d$ is the average spacing between lines. This is related to the so-called *equivalent width* of a line $W_j(X)$ by $W_j(X) = \bar{A}_j d$, where the expression for $W_j(X)$ is exactly the same as given by Eq. (2.16). Thus,

$$W_j(X) = A_j(X) = \int_{-\infty}^{\infty} A_j(\kappa_{\omega j} X)\, d(\omega - \omega_j) = \bar{A}_j d \tag{2.19}$$

The equivalent width is interpreted as the width of a rectangular line (whose center is totally absorbed) having the same absorption area as that of the actual line.

The mean transmittance of a single line, in a finite wave number interval $D = 2\delta$, may be expressed as

$$\bar{\tau}_{j, D} = \frac{1}{2\delta} \int_{-\delta}^{+\delta} \exp(-\kappa_{\omega j} X)\, d(\omega - \omega_j) \tag{2.20}$$

where $\delta$ is the wave number interval from the center of the line. The mean absorption over this interval, therefore, becomes

$$\bar{A}_{j, D} = 1 - \bar{\tau}_{j, D} = \frac{1}{\delta} \int_{0}^{\delta} [1 - \exp(-\kappa_{\omega j} X)]\, d(\omega - \omega_j) \tag{2.21}$$

Note that $\bar{\tau}_{j, D}$ and $\bar{A}_{j, D}$ are in nondimensional form.

### *2.1. Radiative Transmittance by Spectral Lines*

For a homogeneous atmosphere, the radiative transmittance of a line with Lorentz profile is obtained by combining Eqs. (2.4) and (2.14) as

$$\tau_{\omega j} = \tau_L(\omega) = \exp[-2x/(y^2 + 1)] = \tau_L(x, y) \tag{2.22}$$

where

$$x = S_j X / 2\pi\gamma_L \qquad y = (\omega - \omega_j)/\gamma_L$$

It should be noted that, for large $y$ (i.e., away from the line center), Eq. (2.22) approaches to unity for all $x$ while for small $x$ it approaches to unity for all $y$.

The transmittance of a Doppler-broadened line is obtained by combining Eqs. (2.11) and (2.14) as

$$\tau_{\omega j} = \tau_D(\omega) = \exp[-x_D \exp(-v^2)] = \tau_D(v, x_D) \tag{2.23a}$$

where

$$x_D = \kappa_0 X = [(S_j/\gamma_D)(\ln 2/\pi)^{1/2}]X$$

represents the optical path at the line center. For large $v$ (i.e., away from the line center), the transmittance approaches a value of unity, while in the vicinity of the line center it may be expressed by

$$\tau_D(\omega) = \exp(-x_D) \tag{2.23b}$$

As in the case of the Lorentz line profile, $\tau_D(\omega)$ also approaches a value of unity in the linear limit.

The transmittance of a combined Lorentz-Doppler (Voigt) line profile is obtained by combining Eqs. (2.10) and (2.14) as

$$\tau_{\omega j} = \tau_V(\omega) = \exp(-x_D K(a, v)) = \tau_V(a, v, x_D) \tag{2.24}$$

Note that the transmittance of a Voigt line profile also approaches unity in the linear limit. It can be shown that Eq. (2.24) reduces to the Lorentzian case for large $a$ and to the Doppler case in the limit of small $a$.

The transmittance by the Lorentz line profile, Eq. (2.22), can be expressed in terms of the quantities $x_D$, $a$, and $v$ as

$$\tau_L(\omega) = \exp\{-x_D[(a/\sqrt{\pi})/(v^2 + a^2)]\} = \tau_L(a, v, x_D) \tag{2.25}$$

For transmittance at the line center, this can be written as

$$\tau_L(a, x_D) = \exp(-x_D/a\sqrt{\pi}) \tag{2.26}$$

Equation (2.25) is a convenient expression for comparing the results with the transmittance of the Doppler and Voigt line profiles.

The transmittance of the three line profiles (Lorentz, Doppler, and Voigt) at the line center are illustrated in Fig. 2 for various values of the parameter $a$. As would be expected, for $a = 0 \rightarrow 0.1$, the Voigt line transmittance is analogous to that given by the Doppler line profile. For values of $a \geq 5$, the transmittance by Lorentz and Voigt lines is identical for all path lengths.

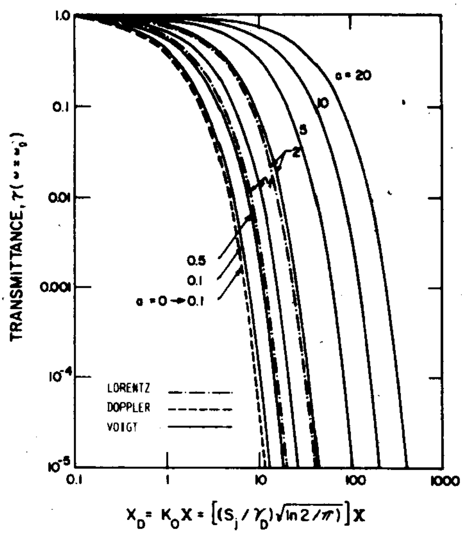


FIG. 2. Transmittance of Lorentz, Doppler, and Voigt lines evaluated at the line center.

Comparisons of the transmittance by the three line profiles are also shown in Figs. 3 and 4 for $x_D = 10$ and for values of $a$ equal to 0.1 and 1, respectively. It should again be noted that at $a = 0.1$, the transmittance of a Voigt line can be approximated quite accurately by the transmittance of a Doppler line. At $a = 1$, however, the transmittance by the Lorentz line provides a better approximation for the Voigt line transmittance.

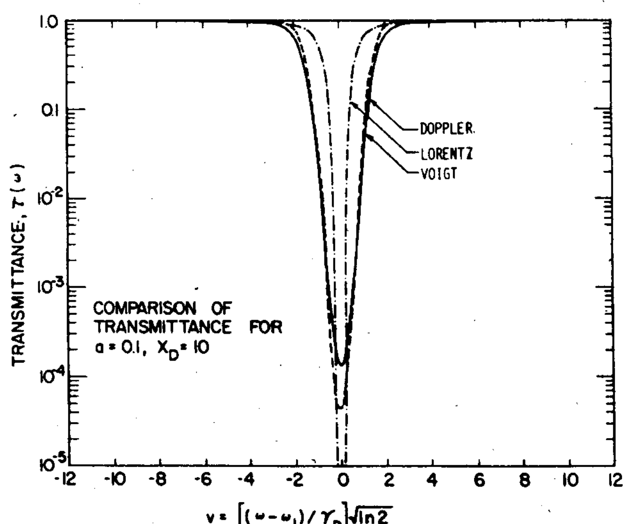


FIG. 3. Comparison of transmittance for $a = 0.1$ and $x_D = 10$.