REFRACTIVE INDEX OF GASEOUS MIXTURES IN THE LORENTZ-LORENZ SPECTROSCOPY

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In this paper we present the expressions that have been derived using the Lorentz–Lorenz formula of the dispersion theory and which enable one to calculate the real and imaginary parts of the dielectric constant and refractive index of an arbitrary gaseous mixture. The calculations use experimental data on the absorption spectra of the mixture. These values may be calculated as functions of the incident radiation frequency, including spectral regions involving the absorption lines and bands.

We have shown in our study that the absorption line contour that follows from the dispersion theory does not coincide with the Lorentz contour. We propose that the line contour considered in this paper be called as the Lorentz–Lorenz contour to distinguish it from the Lorentz one.

The dielectric constant and related to it refractive index of any medium, including the atmosphere, is not a constant value. These quantities are functions of an electromagnetic wave frequency, propagated through the medium. The change in the refractive index value with changing frequency (or wavelength) of the radiation is known as the dispersion phenomenon.

The dispersion phenomenon has been investigated quite thoroughly[1] for the electromagnetic waves from the optical range. For this spectral range simple formulae were obtained by Cauchy, Sellmeyer, Koch, Edlen, Barella-Sirs, and others that allow one to calculate the refractive index of a medium as a function of the radiation frequency. In other spectral regions the frequency dependence of the refractive index has been studied experimentally outside the absorption bands and mainly for standard gaseous mixtures. However, the needs of rapidly developing laser optics, including atmospheric optics, being first of all motivated by the necessity to develop new and highly sensitive methods of laser monitoring of the environment, stimulate obtaining formulae that could provide for calculating the dispersion of arbitrary gaseous media and in the spectral regions that may involve both isolated absorption lines and groups of lines.

In this paper we present the expressions that have been derived using the Lorentz-Lorenz formula of the dispersion theory[1–4] and which enable one to calculate the real and imaginary parts of the dielectric constant and refractive index of an arbitrary gaseous mixture. The calculations use experimental data on the absorption spectra of the mixture. These values may be calculated as functions of the incident radiation frequency, including spectral regions involving the absorption lines and bands.

To describe the dispersion rigorously, it is necessary to use quantum theory of the atomic structure of the matter.[5–10] However, a simplified model of the dispersive media can be constructed based on the classical theory of electromagnetic waves. Since the results of classical and quantum theories practically coincide,[1] we shall consider the dispersion phenomenon following mainly Refs. 1–4.

The substance of a medium is considered as a combination of interacting particles (atoms and molecules), that can be polarized under the action of an external electromagnetic field and, hence, gain electric and magnetic moments. The dipole electric moment of each molecule, induced by the external field, is considered to be proportional to the effective electric field with the proportionality coefficient α_E called the polarizability. If being interested only in the effect, averaged over all possible orientations of the molecules, one may derive the expression that relates the dielectric constant of a medium, ε, with its mean polarizability α_E

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} N \alpha_E , \qquad (1)$$

where N is the number of molecules per unit volume. The formula (1) is the so-called Lorentz–Lorenz formula and it serves as the bridge connecting the phenomenological Maxwell electromagnetic theory with the theory of atomic structure of the matter. The Lorentz–Lorenz formula is the basic formula of the dispersion theory.

From Eq.(1) follows an explicit expression for ε:

$$\varepsilon = \frac{1 + 8\pi\, N\, \alpha_E / 3}{1 - 4\pi\, N\, \alpha_E / 3} \,,\; \varepsilon - 1 = \frac{4\pi\, N\, \alpha_E}{1 - 4\pi\, N\, \alpha_E / 3} \,. \qquad (2)$$

When estimating the dipole moment of a molecule induced by an external field, it is necessary to know the value of a deviation, $r = (x, y, z)$, of each charged particle in the molecule, for example electrons from the relevant equilibrium position. The exact determination of the effective displacement of electrons and nuclei of a molecule under the effect of electric field is too a complicated problem of quantum mechanics.[5–10] However, it is possible to consider that, with a good approximation (and it is confirmed by the rigorous theory), the electrons behave so as, if at their deviation from the equilibrium position, they undergo the action of a quasi-elastic restoring force $F_b = -qr$, where q is the quasi-elasticity factor of an oscillator. Therefore, if e is the electron charge and m is the electron mass, then the equation of electron motion can be written in the following form[1]:

$$m\,\frac{d^2 r}{dt^2} + g\,\frac{dr}{dt} + qr = eE' \,,$$

where t is time, e' is the effective electric field that influences the molecule, and g is the damping factor of the oscillator. In the general case the equation of motion has a more complicated form. The equation may be modified based on the experimental data compiled up to now on the absorption of electromagnetic waves in different media. However, this equation is quite suitable for our purposes, and, as shown below, the results obtained using it are in a good agreement with the experiment.

Considering further the effective field e' as a harmonic field with the angular (cyclic) frequency ω, we obtain the solution $r(\omega)$ of the equation of motion. This solution describes the dipole moment, $er(\omega)$, of each electron which it contributes into the medium polarization. Assuming, that in each molecule there is only one effective electron (oscillator), for the mean polarizability α_E we obtain the following expression:

$$\alpha_E = \alpha_E(\omega) = \frac{e^2}{m(\omega_0^2 - \omega^2) - \mathbf{i}\,\omega\, g} \,,\; \omega_0 = \sqrt{q/m} \,, \quad (3)$$

where ω_0 is the resonance frequency of the oscillator in the absence of radiation attenuation.

By substituting Eq. (3) into Eq. (2) and introducing the dimensionless parameters, we obtain the dependence of the dielectric constant $\varepsilon = \varepsilon(\omega)$ on the frequency ω of radiation, propagated through the medium

$$\varepsilon(\omega) - 1 = C_N\, E\left(\frac{\omega}{\omega_*}, \frac{g}{m\,\omega_*}\right) \,; \qquad (4)$$

$$E(x, y) = \frac{1}{1 - x^2 - \mathbf{i}yx} \,;\quad \omega_* = \omega_0 \sqrt{1 - c_0} \,;$$

$$q_N = \frac{3c_0}{1 - c_0} \,,\quad c_0 = \frac{4\pi e^2\, N}{3m\omega_0^2} = \frac{4\pi e^2\, N_A}{3m\omega_0^2 W}\, \rho_* \,.$$

We use here the equality $N = N_A \rho_* / W$, where $N_A = 6.02 \cdot 10^{23}$ is the Avohadro number and equals to the number of molecules in one mole, W is the molecular weight of the medium substance, and ρ_* is the substance density. The value ω_* in Eq. (4) has the meaning of a shifted resonance frequency that corresponds to the resonance frequency for the dielectric constant, as is seen from Eqs. (2) and (3). Because we have that $e(0, y) = 1$, in Eq.(4), the constant q_N determines the static value of the dielectric constant (at zero frequency): $\varepsilon(0) = q_N + 1$. Let us note, that normally for gases $c_0 \ll 1$, and therefore, $q_N \ll 1$.

If to introduce into consideration the spatial frequency of radiation ν (the spectroscopic wavenumber), defined by the relation $\nu = 1/\lambda$, where λ is the current wavelength, then the equality $\omega = 2\pi c\nu$ (c is the speed of light) is fulfilled, and Eq. (4) takes the form, which usually used in the spectroscopy

$$\varepsilon(\nu) - 1 = C_N\, E(\nu/\nu_*, \gamma) \,; \qquad (5)$$

$$\nu_* = \omega_*/(2\pi c) \,;\quad \gamma = g/(2\pi c m \nu_*).$$

By presenting ε as $\varepsilon = \varepsilon_R + \mathbf{i}\,\varepsilon_I$ and separating the real and imaginary parts of Eq. (5), we obtain

$$\varepsilon_R - 1 = C_N\, E_R(\xi, \gamma),\; \varepsilon_I = C_N\, E_I(\xi, \gamma) \,,\; \xi = \nu/\nu_*, \quad (6)$$

$$E_R(\xi, \gamma) = \frac{1 - \xi^2}{(1 - \xi^2)^2 + \gamma^2 \xi^2} \,,$$

$$E_I(\xi, \gamma) = \frac{\gamma\xi}{(1 - \xi^2)^2 + \gamma^2 \xi^2} \,.$$

As seen from Eq. (6), functions $e_R(\xi, \gamma)$ and $e_I(\xi, \gamma)$ describe the frequency dependence of real and imaginary parts of the dielectric constant of the medium. As shown below, the function $e_R(\xi, \gamma)$ describes the frequency dependence of the real part of the refractive index, that determines the refractive properties of the medium, and $e_I(\xi, \gamma)$ describes the frequency dependence of the imaginary part that characterizes the absorption properties of the medium. Because of the importance of these functions, let us analyze their behavior depending on the values of the parameters ξ and γ.

Analysis of the function $e_R(\xi, \gamma)$ shows, that for the argument ξ from the interval $0 \le \xi < \infty$ it has two extrema: the maximum at the point $\xi = \xi_{max}$ and the minimum at the point $\xi = \xi_{min}$, where

$\xi_{max} = \sqrt{1 - \gamma}$ at $\gamma \leq 1$, $\xi_{min} = \sqrt{1 + \gamma}$.

At the extremum points the function e_R has the values

$$E_R(\xi_{max}, \gamma) = 1/[\gamma(2 - \gamma)] , \quad \gamma \leq 1 , \qquad (7)$$

$$E_R(\xi_{min}, \gamma) = - 1/[\gamma(2 + \gamma)] .$$

In the intervals between the extremum points the function e_R may be presented by the following asymptotic expressions:

$$e_R(\xi, \gamma) = \begin{cases} 1 + \xi^2 (1 - \gamma^2) , & 0 \leq \xi \ll a_1, \\ 2\gamma^{-2}(1 - \xi) [1 + 2(1 - \xi)] , & a_1 \ll \xi \ll a_2, \\ -\xi^{-2} [1 + \xi^{-2} (1 - \gamma^2)] , & a_2 \ll \xi < \infty; \end{cases}$$
$$(8)$$

$a_1 = \sqrt{1 - \gamma} \ \theta(1 - \gamma), a_2 = \max [1, | \gamma^2 - 2 |^{+1/2}],$

$\theta(x) = 1$ at $x \geq 0$, $\theta(x) = 0$ at $x < 0$.

From these expressions it follows, that in the range of small values of the parameter ξ ($\xi \ll 1$), the function $e_R(\xi, \gamma)$, that describes the frequency dependence of the real refractive index of the medium, increases with the increasing ξ (with the increase of the frequency ν), starting from its value at zero frequency $e_R(0, \gamma) = 1$. At large ξ values ($\xi \geq \xi_{min}$) the function $e_R(\xi, \gamma)$ also increases with increasing ξ and $e_R(\xi, \gamma) \to 0$ at $\xi \to \infty$, remaining negative in the given interval. It is said that in these cases we deal with the normal dispersion.

In the vicinity of the point $\xi = 1$, that corresponds to the shifted resonance frequency $\nu = \nu_*$, the function e_R decreases from $e_R(\xi_{max}, \gamma)$ down to $e_R(\xi_{min}, \gamma)$ with increasing ξ, passes through zero value at the point $\xi = 1$ (where $e_R(1, \gamma) = 0$). In this case it is said we deal with the anomalous dispersion. In the region of the anomalous dispersion the rate of the function e_R decrease depends on the value of the parameter γ. At small γ values ($\gamma \ll 1$) the rate of the function e_R decrease is maximum and decreases with increasing γ parameter. At $\gamma \to \infty$ the absolute values of $e_R(\xi_{max}, \gamma)$ and $e_R(\xi_{min}, \gamma)$ decrease and the maximum value of e_R degenerates.

The function $e_I(\xi, \gamma)$ has one maximum at the point $\xi = \xi_c$

$$\xi_c = \sqrt{-(\gamma^2 - 2)/6 + \{[(\gamma^2 - 2)/6]^2 + 1/3\}^{1/2}} ,$$

which takes the value

$$E_I(\xi_c, \gamma) = \gamma/[2\xi_c (\gamma^2 - 2 + 2\xi_c^2)] . \qquad (9)$$

Thus, for small γ values, ($\gamma \ll 1$), that normally occur in practice, we have

$\xi_c = 1 - \gamma^2/8$, $E_I(\xi_c, \gamma) = 1/\gamma$.

The passage to the regions of small and large ξ values leads to a decrease in the function e_I down to zero: $e_I(\xi, \gamma) \to 0$, at $\xi \to 0$, and at $\xi \to \infty$. To the left and to the right of the point of maximum, and also in its vicinity, e may be presented by the following asymptotic expressions:

$e_I(\xi, \gamma) =$

$$= \begin{cases} \gamma\xi[1 + \xi^2(2 - \gamma^2)], & 0 \leq \xi \ll b_1, \\ E_I(\xi_c, \gamma)[1 - (\xi - \xi_c)^2/(2\gamma_c^2)], & |\xi - \xi_c| \ll \gamma_c \sqrt{2}, \\ \gamma\xi^{-3}[1 + \xi^{-2} (2 - \gamma^2)], & b_2 \ll \xi < \infty ; \end{cases}$$
$$(10)$$

$\gamma_c^2 = \xi_c^2(\gamma^2 - 2 + 2\xi_c^2) /(\gamma^2 - 2 + 6\xi_c^2)$,

$b_1 = \min [1, |\gamma^2 - 2|^{-1/2}]$,

$b_2 = \max [1, |\gamma^2 - 2|^{+1/2}]$.

The form of function $e_I(\xi, \gamma)$, that describes the frequency behavior of the absorption properties of the medium, shows, that in the vicinity of the shifted resonance frequency $\nu \sim \nu_*$ ($\xi \sim \xi_c$) the absorption reaches its maximum (maximum of the absorption at $\xi = \xi_c$) and decreases as ν deviates from ν_*. In this case it is said that there is an absorption line with the center at the frequency $\nu_c = \nu_* \xi_c$. As was shown above, for small γ values ($\gamma \ll 1$), that only are of practical interest, the value ξ_c may be assumed to be equal to unity, that corresponds to the frequency of the absorption line center, $\nu_c = \nu_*$.

As follows from Eq. (10) the parameter γ_c characterizes the halfwidth, over the variable ξ, of the function $e_I(\xi, \gamma)$ at the half maximum level, $e_I(\xi_c, \gamma)/2$, and is called the halfwidth of an absorption line. One can see from Eq. (10) that at small γ values ($\gamma \ll 1$), $2\gamma_c = \gamma/2^{1/2}$. Besides, if one considers the central asymptotics (10) being acceptable up to the boundaries of its applicability shown in Eq. (10), then $e_I(\xi_c + \gamma/2, \gamma) = 0$. Therefore, the parameter γ in the function $e_I(\xi, \gamma)$ has the meaning of the absorption line width. Let us note, that both γ_c, and γ characterize the size of the function $e_I(\xi, \gamma)$ at the variation of the normalized variable $\xi = \nu/\nu_*$. Therefore, for non-normalized variable ν (in the frequency domain) the halfwidth and the width of an absorption line are represented as $\gamma_c \nu_*$ and $\gamma \nu_*$, respectively.

The amplitude of the line is usually termed as its intensity and is designated as S. As seen from Eqs. (6), (9) and (10), $S = q_N e_I(\xi_c, \gamma)$ and, therefore, for small γ values ($\gamma \ll 1$) the intensity of an absorption line is proportional to q_N, while being inversely proportional to its width, γ ($S = q_N/\gamma$).

In optics the refractive index n is often used instead of the dielectric constant ε. For nonmagnetic substances, ε and n are connected by the Maxwell relation $n^2 = \varepsilon$. Since ε is a complex value

$(\varepsilon = \varepsilon_R + \mathbf{i}\varepsilon_I)$, then the refractive index n is also a complex value. Designating the real part n as n_R, the imaginary part as n_I $(n = n_R + \mathbf{i}\, n_I)$, we obtain, from the Maxwell relation, that

$$n_R^2 = (\varepsilon_R + \sqrt{\varepsilon_R^2 + \varepsilon_I^2})/2 \ , \ \ n_I^2 = \varepsilon_I^2/(4\, n_R^2) \ , \qquad (11)$$

where ε_R and ε_I are defined by the equalities (6). If the medium is a gas and, therefore, in Eq. (6) $q_N \ll 1$, then for q_N values that satisfy the inequality $q_N\, e_I(\xi_c, \gamma) \ll 1$, expressions (11) can be reduced to a simpler form

$$n_R = \sqrt{\varepsilon_R} \ , \quad n_I = \varepsilon_I/2 \ . \qquad (12)$$

The functions $(n_R - 1)/q_N$ and n_I/q_N, obtained numerically by formulae (11) for the values $\gamma = 0.1$ and q_N from the domain $q_N\, e_I(\xi_c, \gamma) \ll 1$, are shown in Fig. 1. As the quantities ε_R and ε_I entering Eq. (12) are represented by the equalities (6), then at $q_N\, e_I(\xi_c, \gamma) \ll 1$ we have, from Eq. (12), that

$$n_R = \sqrt{1 + C_N\, E_R} \approx 1 + C_N\, E_R/2 \ ,$$

$$n_I = C_N\, E_I/2 \ ,$$

$$(n_R - 1)/C_N = E_R/2 \ , \quad n_I/C_N = E_I/2$$

and, therefore, the plots depicted in Fig. 1 are the graphical representations of functions $e_R/2$ and $e_I/2$, simultaneously.
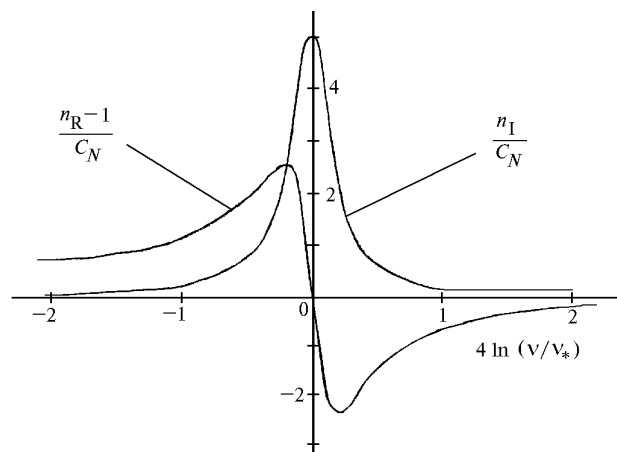

FIG. 1. *Dependence of the complex refractive index* $n = n_R + \mathbf{i}\, n_I$ *on the radiation frequency* ν; ν_* *is the resonance frequency, and* $C_N = n_R^2(0) - 1$.

The above formulae describe the situation, where the medium consists of molecules, each having only one resonance frequency. In the general case there are many such frequencies even in the case of a system of molecules of same kind. Then one is forced to replace expressions for both the mean polarizability α_E,

(formula (3)), and $\varepsilon(\omega)$ (in Eq. (4)) by the more general expressions.[1] For the system of molecules of same kind we obtain the following relationship instead of Eq. (3)

$$\alpha_E(\omega) = \sum_k \frac{e_k^2\, f_k}{m_k\, (\omega_k^2 - \omega^2) - \mathbf{i}\omega g_k}, \ \omega_k = \sqrt{q_k/m_k} \ , \ (13)$$

where the index k denotes physical parameters of the kth virtual oscillator. The value Nf_k (N is the number of molecules per unit volume) equals to the number of oscillators for the relevant resonance frequency ω_k.

The equation (1) remains yet applicable, but now the electrons, groups of electrons, the nuclei of atoms, and so on, are to be considered as oscillators. The number of these oscillators is very large. However, in the majority of cases only a finite number of values f_k, noticeable magnitudes,[1] whereas other values may be neglected. The entire formal theory is almost unchanged when introducing the quantum-mechanics rules, but it already allows one to calculate the values f_k for a particular electron system.

For the system of molecules of different kinds the summation in Eq. (13) should be extended to the resonance frequencies of all molecules, including the frequencies, activized at the presence of other molecules. In this case Eq. (1) is used in the following form:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} \sum_j N_j\, \alpha_{Ej}(\omega) \ , \qquad (14)$$

where the summation is being done over all kinds of molecules, $\alpha_{Ej}(\omega)$ is the polarizability of molecules of the jth kind, given by the expression (13), in which the set of parameters, that depend on the summation index k, changes at changing the kind of molecules (change of the number j), N_j is the number of molecules of the jth kind per unit volume.

Let the medium, in Eq. (14), be first composed of the molecules of two kinds:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} N_1\, \alpha_{E1}(\omega) + \frac{4\pi}{3} N_2\, \alpha_{E2}(\omega) \ . \qquad (15)$$

Let us designate the dielectric constants of the media as ε_1 and ε_2 for the molecules of the kind 1 and 2, respectively. The equations analogous to Eq. (1) are valid for ε_1 and ε_2

$$\frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} = \frac{4\pi}{3} N_1\, \alpha_{E1}(\omega) \ ,$$

$$\frac{\varepsilon_2 - 1}{\varepsilon_2 + 2} = \frac{4\pi}{3} N_2\, \alpha_{E2}(\omega) \ , \qquad (16)$$

the solutions to which are the relevant Lorentz-Lorenz formulae.

$$\varepsilon_1 - 1 = \frac{4\,\pi\,N_1\,\alpha_{E1}}{1 - 4\,\pi\,N_1\,\alpha_{E1}/3}\,,$$

$$\varepsilon_2 - 1 = \frac{4\,\pi\,N_2\,\alpha_{E2}}{1 - 4\,\pi\,N_2\,\alpha_{E2}/3}\,.$$

The equation (15), whose right-hand side is the sum of two terms, has an exact solution, expressed through the dielectric constants ε_1 and ε_2. This solution can be presented as follows:

$$\varepsilon - 1 = \frac{(\varepsilon_1 - 1) + (\varepsilon_2 - 1) + (2/3)\,(\varepsilon_1 - 1)\,(\varepsilon_2 - 1)}{1 - (1/9)\,(\varepsilon_1 - 1)\,(\varepsilon_2 - 1)}. \tag{17}$$

In the case of gases we have that $|\varepsilon_1 - 1| \ll 1$, $|\varepsilon_2 - 1| \ll 1$ and, therefore, it is possible to neglect the terms of the second order of smallness in Eq. (17). In this case we obtain from Eq. (17) that

$$\varepsilon - 1 = \sum_{j=1}^{2} (\varepsilon_j - 1)\,. \tag{18}$$

For three components in the right-hand side of equation (14) it is possible to take the dielectric constant of the mixed medium (Eq. (18)) of molecules of the kinds 2 and 3 to be ε_2. As a result the term $\varepsilon_2 - 1$ in Eq. (18), will itself be presented as a sum of two terms after performing the operations analogous to those according to the procedure (15)−(18)

$$(\varepsilon_2 - 1) \rightarrow \sum_{j=2}^{3} (\varepsilon_j - 1)\,,$$

where the values ε_2 and ε_3, in the right-hand side of this expression, denote the dielectric constants of the media, involving separately the molecules of the kinds 2 and 3. Continuing this procedure, the summation in Eq. (18) can be used for all kinds of molecules in the system considered, and to all resonance frequencies, characteristic of each kind. Then

$$\varepsilon - 1 = \sum_{j} \sum_{k} (\varepsilon_{jk} - 1)\,, \tag{19}$$

where ε_{jk} is the dielectric constant of the medium involving only the molecules of the jth kind, for which we take into consideration only one resonance frequency with the number k. The value ε_{jk} is set by the formulae (4) and (5), in which it is necessary to denote the physical parameters of an oscillator e, m, g, q, and the related to those parameters ω_0, ω_*, ν_*, γ, q_N, by the indices jk and by the index j the parameters of the medium N, W, ρ_*. Thus the values c_0 and q_N in Eq. (4) transform according to the rules

$$c_0 \rightarrow c_{0jk} = \frac{4\pi e_{jk}^2\,N_A\,f_{jk}}{3\,m_{jk}\,\omega_{0jk}^2\,W_j}\,\rho_{*j}\,,$$

$$C_N \rightarrow C_{Njk} = \frac{3\,c_{0jk}}{1 - c_{0jk}} \approx 3\,c_{0jk}\,,$$

where ρ_{*j} is the density of a medium involving the molecules of the jth kind, or the partial concentration of jth molecular component of the mixture, f_{jk} is the parameter analogous to f_k in Eq. (13) and it denotes the specific weight of kth resonance frequency in the polarizability of the jth medium.

After performing the above operations, we find for the dielectric constant of a multicomponent gaseous medium that

$$\varepsilon - 1 = \sum_{j} \sum_{k} C_{Njk}\,E(\nu/\nu_{*jk}, \gamma_{jk}), \tag{20}$$

where the function $e(x, y)$ is defined by Eq. (4).

Representing ε again as $\varepsilon = \varepsilon_R + \mathbf{i}\varepsilon_I$ and separating the real and imaginary parts in Eq. (20), we have

$$\varepsilon_R - 1 = \sum_{j} \sum_{k} C_{Njk}\,E_R(\nu/\nu_{*jk}, \gamma_{jk}),$$

$$\varepsilon_I = \sum_{j} \sum_{k} C_{Njk}\,E_I(\nu/\nu_{*jk}, \gamma_{jk}). \tag{21}$$

Here the functions $e_R(x, y)$ and $e_I(x, y)$ are defined by the relations (6).

Using Eq. (21), it is possible to obtain the expressions for real n_R and imaginary n_I parts of the refractive index n ($n = n_R + \mathbf{i}\,n_I$) of a multicomponent gaseous medium. Using Eqs. (12) and (21), we obtain

$$n_R - 1 = \frac{1}{2} \sum_{j} \sum_{k} C_{Njk}\,E_R(\nu/\nu_{*jk}, \gamma_{jk}),$$

$$n_I = \frac{1}{2} \sum_{j} \sum_{k} C_{Njk}\,E_I(\nu/\nu_{*jk}, \gamma_{jk}). \tag{22}$$

If the values of the parameters ν_{*jk}, γ_{jk}, and q_{Njk} are known, the relations (22) allow one to calculate the real and imaginary parts of the refractive index of the medium as functions of the incident radiation frequency ν. However, as was already mentioned, even for simple molecular systems the evaluation of values of these parameters is not so simple being quite a laborious problem. In practice it is easier to find the values of these parameters from a comparison between theoretical and experimental data on n_I (or n_R) and then to use these values in calculation of the values n_R (or n_I).
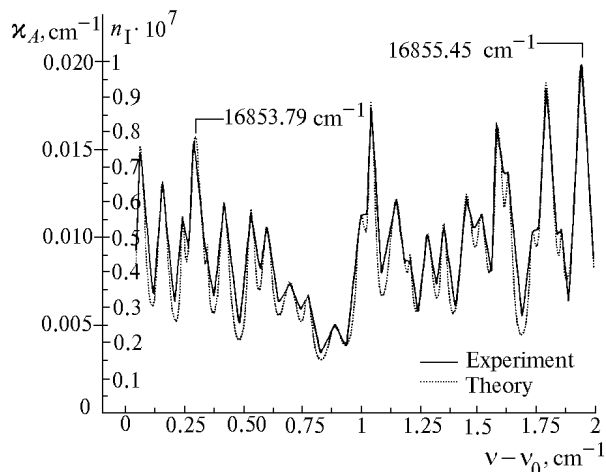
FIG. 2. Comparison of theoretical and experimental data on spectral absorptance of nitrogen dioxide: $\varkappa_A$ is the spectral absorptance, n_I is the imaginary part of the refractive index, $\varkappa_A = 4\pi\nu n_I$, $\nu = 1/\lambda$, $\nu_0 = 16853.50$ cm^{-1}, the absorptance of NO_2, recorded at the pressure of 667 Pa, Ref. 10, (solid line), and the absorptance, calculated by the formulae (22) and (23) using parameters of the absorption lines, being a solution to the set of equations (24) (dotted line).

Figure 2 shows the results of the comparison made between theoretical and experimental data on the imaginary part of the refractive index of the medium n_I. The values of parameters ν_{*jk}, γ_{jk}, and q_{Njk}, that have been sought from the comparison with experimental values, are given in Table I. Then we have used these values for calculating the frequency dependence of the real part of the refractive index of the medium n_R. The dependence of n_R on the radiation frequency is shown in Fig. 3.

For the experimental data we took a portion of data from Ref. 10 on the absorption spectrum of nitrogen dioxide (NO_2) in the wavelength region of incident radiation at 0.59 μm. The spectrum of NO_2 has been recorded in the mixture of NO_2 and O_2 at a rather low total pressure of the mixture of 667 Pa. The number of NO_2 molecules per unit volume was $N = 1.7 \cdot 10^{17}$ cm^{-3}. The spectrum has been recorded with a laser opto-acoustic spectrometer of an ultra-high spectral resolution of 0.0007 cm^{-1}. The error in the position of the absorption line centers determined was below 0.01 cm^{-1}. As compared to the known atlas of the NO_2 absorption spectrum,[11] the spectrum from Ref. 10 has been obtained with a higher resolution and contains more lines. The width of the spectral interval, used in the comparison, is about 2 cm^{-1} from 16853.50 and to 16855.45 cm^{-1} (593.349−593.280 nm). This interval contains no less than 20 absorption lines recorded.

TABLE I. Values of the parameters of absorption lines, obtained by solving the set of equations (24).

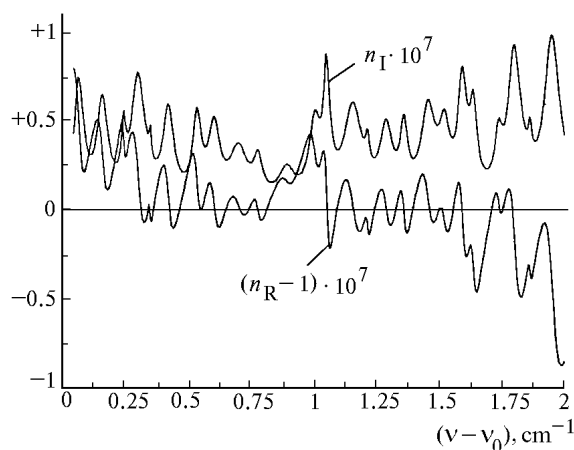| **	Frequency of the line center ν_*, $\nu_* - \nu_0$, cm^{-1} $\nu_0 = 16853.50$ cm^{-1}	Intensity of the line S for ε_I ($S = q_N/\gamma$), $S \cdot 10^{+7}$	Width of the line γ, $\gamma \cdot 10^{+6}$	Parameter q_N, $q_N \cdot 10^{+13}$
1	0.066	1.386	2.705	3.748
2	0.160	1.122	3.117	3.499
3	0.244	0.603	1.181	0.712
4	0.302	1.424	3.904	5.559
5	0.349	0.313	0.547	0.171
6	0.422	0.997	3.067	3.058
7	0.535	0.898	2.431	2.183
8	0.602	0.807	3.159	2.549
9	0.699	0.575	5.208	2.992
10	0.777	0.407	2.524	1.027
11	0.890	0.329	4.475	1.474
12	1.003	0.825	3.248	2.680
13	1.051	1.324	1.825	2.416
14	1.155	1.051	5.143	5.408
15	1.213	0.329	1.041	0.343
16	1.287	0.763	3.481	2.658
17	1.358	0.735	2.099	1.543
18	1.455	0.987	4.030	3.979
19	1.520	0.695	2.943	2.046
20	1.592	1.270	2.592	3.292
21	1.636	0.896	1.991	1.783
22	1.736	0.542	2.059	1.116
23	1.801	1.636	3.735	6.112
24	1.862	0.362	0.976	0.353
25	1.953	1.852	4.591	8.504

** the number of the absorption line

FIG. 3. Complex refractive index of nitrogen dioxide $n = n_R + i\, n_I$ in the spectral region $16853.50 - 16855.45$ cm^{-1}, $\nu_0 = 16853.50$ cm^{-1}, calculation by formula (22) for the parameters of the absorption lines being a solution to the set of equations (24), n_R is the real and n_I the imaginary parts of the refractive index.

To make a comparison with the theoretical results, the coefficient of spectral absorptance $\varkappa_A(\nu)$, taken from Ref. 10, and being the proportionality constant in the Bouguer law written in the differential form, has been used to calculate the imaginary part of the refractive index with the help of the following relations:

$$\varkappa_A(\nu) = k\,\varepsilon_I(\nu) = 2k\,n_I(\nu) ,$$

$$k = 2\pi/\lambda = 2\pi\nu , \qquad (23)$$

where k is the wavenumber of radiation in vacuum. The expression (23) is valid for short paths, that are commonly in use when measuring the absorption spectra under laboratory conditions.

Since we consider only the absorption spectrum of NO_2, it is possible to consider the medium as a single-component one, and to remove the summation over j in Eq. (22) and omit index j. The reconstruction of the parameters ν_{*k}, γ_k, and q_{Nk} has been carried out by numerically solving the system of nonlinear equations

$$n_I(\nu_m) = \frac{1}{2} \sum_{k=1}^{M} C_{Nk}\,E_I(\nu_m/\nu_{*k}, \gamma_k) ,$$

$$1 \le m \le 3\,M , \qquad (24)$$

where l is the number of the absorption lines in the spectral region considered. As ν_m we used the values of frequencies that correspond to the extremum points in the experimental absorption spectrum (maximum, right or left minimum, and an intermediate point between them for each line). The values of parameters ν_{*k}, γ_k, and q_{Nk} ($1 \le k \le l$), obtained as a result of solving the set of equations (24), are given in Table I.

The imaginary part of the refractive index $n_I(\nu)$, calculated using the values ν_{*k}, γ_k, and q_{Nk} from Table I, is shown in Fig. 2 together with the experimental absorption spectrum for $n_I(\nu)$ (reconstructed from the spectrum of the absorptance $\varkappa_A(\nu)$ by the relation (23)). To compare the experimental absorption spectra $n_I(\nu)$ and $\varkappa_A(\nu)$, the values $\varkappa_A(\nu)$ are given in Fig. 2 at the parallel ordinate axis.

As seen from Fig. 2, there is quite good agreement between the theory and experiment. The difference between theoretical and experimental data is observed only at the spectrum minima and that does not exceed 16%. From Fig. 3 it follows also, that the frequency dependence of the real part of the refractive index n_R, calculated for parameters from Table I (ν_{*k}, γ_k, and q_{Nk}), as well as the dependence of the imaginary part, have a fine structure. Thus, the deviation of the value n_R from unity can be both positive and negative.

The comparison made here between theoretical and experimental data on the imaginary part of the refractive index, n_I, of a medium and the calculations,

made on the basis of this comparison, of the frequency dependence of the real part of the refractive index n_R can be carried out for other spectral regions of the absorption spectrum, other gases, and multicomponent gaseous mixtures as well.

In the gas spectroscopy when studying spectral absorptance the contour of the absorption line is normally that is called the dispersion or the Lorentz one. This contour had been derived within the framework of classical electromagnetic theory with the account for Lorentz-Lorenz formula and was first proposed by Lorentz in Ref. 4. The contour describes the shape of an absorption line caused by collisions among molecules, Refs. 4–10. In modern designations the dispersion (Lorentz) contour has the form

$$\varkappa_L(\nu) = \frac{S_{Li}}{\pi}\,\frac{\gamma_L}{(\nu - \nu_0)^2 + \gamma_L^2} = \frac{S_L\,\gamma_L^2}{(\nu - \nu_0)^2 + \gamma_L^2},$$

$$S_{Li} = \int_0^\infty \varkappa_L(\nu)\,d\nu , \quad S_L = \varkappa_L(\nu_0) = \frac{S_{Li}}{\pi\,\gamma_L} ,$$

where ν_0 is the frequency of the absorption line center, γ_L is the halfwidth of the line at the level $\varkappa_L(\nu_0)/2$, S_{Li} and S_L are the integral intensity and the intensity of lines, respectively.

The absorption line contour considered in this paper is written for the spectral absorptance, $\varkappa_{LL}(\nu)$. Taking into account the relations (6) and (23), it can be presented in the form

$$\varkappa_{LL}(\nu) = k\,\varepsilon_I(\nu) = 2\pi\,\nu\,C_N\,E_I(\xi, \gamma) ,$$

$$\varkappa_{LL}(\nu) = \frac{S_{LL}\,\gamma_{LL}^2\,\nu^2}{(\nu^2 - \nu_*^2)^2 + \gamma_{LL}^2\,\nu^2} ,$$

$$S_{LL} = \varkappa_{LL}(\nu_*) = 2\pi\,\nu_*\,C_N/\gamma ; \quad \gamma_{LL} = \gamma\,\nu_* .$$

The contours $\varkappa_{LL}(\nu)$ and $\varkappa_L(\nu)$ both have been obtained based on Lorentz-Lorenz formula. However, as it is easy to see, $\varkappa_{LL}(\nu)$ does not coincide with $\varkappa_L(\nu)$. In contrast to Lorentz contour $\varkappa_L(\nu)$, it would be natural to call the contour $\varkappa_{LL}(\nu)$ as Lorentz-Lorenz, and the spectroscopy related to use of the contour $\varkappa_{LL}(\nu)$, as Lorentz-Lorenz spectroscopy.

It is possible to write the expressions (21) and (22) in the form, that contains in an explicit form the concentration of all the molecular components of the mixture. To do this, let us isolate the dependence on the jth component concentration ρ_{*j} from the values q_{Njk}

$$C_{Njk} = c_{jk}\,\rho_{*j} , \quad c_{jk} = \frac{4\,\pi\,e_{jk}^2\,N_A\,f_{jk}}{m_{jk}\,\omega_{0jk}^2\,W_j} . \qquad (25)$$

Substituting Eq. (25) in Eqs. (21) and (22), we have

$$\varepsilon_I = \sum_j \rho_{*j}\, \Phi_{Ij}(\nu)\ , \quad \varepsilon_R - 1 = \sum_j \rho_{*j}\, \Phi_{Rj}(\nu)\ ;$$

$$n_I = \sum_j \rho_{*j}\, \Phi_{Ij}(\nu)/2\ , \ n_R - 1 = \sum_j \rho_{*j}\, \Phi_{Rj}(\nu)/2\ ; \quad (26)$$

$$\Phi_{Ij}(\nu) = \sum_k c_{jk}\, E_I(\nu/\nu_{*jk},\, \gamma_{jk})\ ,$$

$$\Phi_{Rj}(\nu) = \sum_k c_{jk}\, E_R(\nu/\nu_{*jk},\, \gamma_{jk})\ .$$

Let us choose the interval of frequencies, that contains absorption lines of only a concrete jth gaseous component of some mixture. For that interval, where no lines of other components are present, if neglecting the influence of far wings of lines of other ranges,[8] it is possible, in expressions (26), to remove the summation over j and omit the index j. For dielectric constant and the refractive index we obtain from Eq. (26)

$$\varepsilon_I = \rho_*\, \Phi_I(\nu)\ , \quad \varepsilon_R - 1 = \rho_*\, \Phi_R(\nu)\ ;$$

$$n_I = \rho_*\, \Phi_I(\nu)/2\ , \quad n_R - 1 = \rho_*\, \Phi_R(\nu)/2\ . \quad (27)$$

It is easy to see from this expression that in the frequency range chosen both the imaginary part of the dielectric constant (the refractive index) and the deviation of real part from unity are proportional to the partial concentration ρ_* of the gaseous component considered.

Thus, if the laboratory recording of absorption spectra of that or other gas is accompanied by measurements of the density ρ_* or related to it number of molecules per unit volume N (the number density of absorbing molecules), according to Eq. (4), then upon completing the procedure analogous to Eq. (24) on determination of the parameters ν_{*k}, γ_k, and q_{Nk}, the values c_k ($c_k = q_{Nk}/\rho_*$) become known from Eq. (25)

for each line and, therefore, the functions $\Phi_I(\nu)$ and $\Phi_R(\nu)$ are completely determined.

For known functions $\Phi_I(\nu)$, $\Phi_R(\nu)$ the relations (27) enable one to retrieve the concentration of a gaseous species in any gas mixture, for example, in the atmosphere. To do this, at frequencies from the above mentioned interval it is necessary to measure the radiation absorption by the mixture characterized by values ε_I and n_I or the degree of refraction of radiation by the medium, which is described by the values ε_R and n_R.

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