

# PROBLEM OF SPECTRAL LINE PERIPHERY IN ATMOSPHERIC OPTICS

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*Some of the results obtained from solving the problem of spectral line periphery are summarized. Several examples are given to illustrate the potentialities of our line wing theory as applied to important spectroscopic uses in atmospheric optics.*

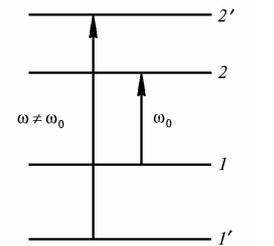
## 1. PHYSICAL PICTURE OF SPECTRAL LINE WINGS

Spectral regions with relatively low molecular absorption are of great importance in atmospheric optics. First, they largely determine the spectrum of the outgoing terrestrial radiation and thereby affect the estimates of the heat balance of the planet. Second, the spectral measurements provide information on the optical properties of aerosol, an important atmospheric constituent which is so changeable that in some cases the data of this type appear to be the only means of its control. Third, it is in these regions where the frequencies are chosen for systems operating through the atmosphere.

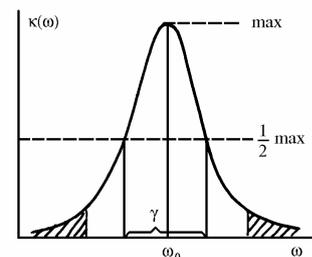
When considering these spectral regions, researchers are faced with nontrivial problems having a long story. The best known example is the problem of the 8–12  $\mu\text{m}$  spectral region concerning the real cause of nonselective attenuation (to stress this fact, the term "continuum" is used) which occurs due to water vapor. This problem will be discussed in Sec. 2. Another example is the long-wave wing of the 4.3  $\mu\text{m}$   $\text{CO}_2$  band which is well-known in practice in connection with observations of rocket flames and in theory, because the well-studied structure of the  $\text{CO}_2$  spectrum makes this wing a "proving ground", in a literal sense of the word, for verification of concepts for a description of the line periphery (see Sec. 3).

Academician V.E. Zuev pointed out these facts as early as 1966 in Ref. 1, where he predicted that the description of the line periphery would undoubtedly lead scientists to seek for new physical ideas. Notably, he made that observation when it was widely believed that the Lorentzian line shape played a pivotal role in atmospheric optics applications. The validity of that prognosis was demonstrated elsewhere<sup>2</sup> and in this paper we will give a short comment.

Figure 1 reminds one of the definitions of the terms used in the discussion below. Levels 1 and 2 of the absorbing ("active") molecule are shifted to positions 1' and 2' due to its collision with a "buffer" molecule to give a certain line shape, i.e. a nonzero absorption coefficient  $\kappa$  at a frequency  $\omega$  different from  $\omega_0$ . The line shape periphery (spectral line wings) is determined by the condition  $\Delta\omega = |\omega - \omega_0| > \gamma$ , where  $\Delta\omega$  is the frequency detuning (see the shaded areas under the curve in Fig. 1b). Peculiarities of the line periphery are entirely related to molecular collisions responsible for the line broadening, because consideration of the Doppler effect is merely a computational problem.



a



b

FIG. 1. On the definition of the line shape,  $\gamma$  is the line halfwidth and  $\omega_0$  is the line center, i.e. transition frequency in an isolated molecule.

The following picture typical of small frequency detuning is well-known. An active molecule interacts vigorously with the field along the free path. However, no absorption of a photon results, for the energy conservation law (the "golden Fermi rule" in terms of quantum mechanics) breaks down here. The collision re-establishes the equilibrium disturbed by the field, brings the molecule back to its initial "low" state, and "transmits" the absorbed photon to the "buffer" molecule, whereas the active molecule leaves the collision to immediately start the cycle again.

At large frequency detunings the active molecule is indifferent to the field within the free path. It is during collision when the conditions for fulfillment of the "golden rule" are set up. Since the absorbed photon is "loaded" on the active molecule, the cycle can be repeated provided

there occurs relaxation process via a number of subsequent collisions. This stage of evolution of the molecule will be termed "drift".

The most remarkable fact is that, in the course of relaxation, the excess internal energy of the molecule gives rise to its directional transfer (a sort of "molecular chaos ordering") for a distance comparable to the wavelength. The long-wave approximation for molecular centers-of-mass, which is generally taken for granted with little or no comment on frequent occasions, is no longer valid. This brings into existence an effect in the imaginary part of the dielectric constant  $\varepsilon$  associated with the absorption coefficient known as spatial dispersion in quantum electrodynamics. The latter implies the relation

$$\mathbf{D}(\mathbf{r}) = \varepsilon' \mathbf{E}(\mathbf{r}) + i \int d\mathbf{r}' f(\mathbf{r}') \mathbf{E}(\mathbf{r} - \mathbf{r}') \quad \text{instead of}$$

$\mathbf{D}(\mathbf{r}) = (\varepsilon' + i\varepsilon'') \mathbf{E}(\mathbf{r})$  between the induction  $\mathbf{D}(\mathbf{r})$  and the field strength  $\mathbf{E}(\mathbf{r})$ . Here  $\varepsilon = \varepsilon' + i\varepsilon''$ , and  $f$  links  $\mathbf{D}$  at a point  $\mathbf{r}$  and the field at other points. Incidentally, in electrodynamics this effect is generally discussed for  $\varepsilon'$  (resulting, for example, in optical activity). Hence, we can speak of a most specific manifestation of the spatial dispersion.

Another factor determining new physical elements in the physical picture of the line periphery is an essential role of the classical (i. e. governing the dynamics of centers-of-mass) intermolecular interaction potential  $V$ . This is in effect made clear by Figure 1. The line wings are formed by collisions at a small intermolecular separation  $R$ , and the Hibbs factor  $z \propto \exp(-V(R)/k\Theta)$  (where  $k$  is the Boltzmann constant,  $\Theta$  is the temperature, and the probability for molecules to be separated by  $R$  is proportional to  $z$ ) is of critical importance for the dependence of  $\kappa$  on temperature and frequency detuning.

These considerations pertaining to the peculiarities of the line periphery were set forth consistently in the monograph<sup>3</sup> edited by V.E. Zuev and subsequently developed, for example, in Refs. 4–7.

A mathematical realization of these ideas implies a certain refinement of the initial expression for the absorption coefficient. In fact, the commonly accepted view is based on the "binary concept", as it is called, wherein the events leading to the spectral line shape take place in a volume with dimensions essentially smaller than the light wavelength. Therefore, the field can be assumed spatially homogeneous, which means the long-wave approximation for the centers-of-mass, and the many-particle aspect of the problem is reduced to a mere counting of the number of collisions. However, as shown in Ref. 4 on the mathematical level of rigor, the long-wave approximation is not valid for a description of the line periphery, and the standard quantum-mechanical calculations of the photon absorption probability must be done again, this time without the long-wave approximation. The resulting expression (within the known factor) has the form:

$$\kappa(\omega) = \text{Re} \int_0^{\infty} dt (\exp(i\omega t)) \text{Tr} A S B \rho S^{-1} B^* \quad (1)$$

The unitary operator  $S$  is the solution of the Schrödinger equation  $i\hbar \partial S / \partial t = H S$ , where  $t$  is time;  $\hbar$  is the Plank constant;  $\rho = (1/Z) \exp(-H/k\Theta)$  is the Hibbs density matrix;  $Z$  is the normalization factor ( $\text{Tr} \rho = 1$ );  $B = M D$ ,  $M$  is the projection of the dipole moment operator of the molecule on the unit vector of polarization of the field,  $D = \exp(i(\omega/c)(\mathbf{k}_0, \mathbf{r}))$ ,  $\mathbf{r}$  is the coordinate of the

center-of-mass of the active molecule,  $\mathbf{k}_0$  is the unit vector of the Poynting vector of the field;

$A = \int d\mathbf{r}' \delta(\mathbf{r}' - \mathbf{r})$  with the integral taken over an elementary volume, and the  $\delta$ -function results from the definition of the dipole moment of the unit volume. In the long-wave approximation  $D = A = 1$ , and Eq. (1) is transformed to a conventional expression for  $\kappa(\omega)$ .

The pragmatic problems behind Eq. (1) are so essential that we have to resort to a trick which might seem strange at first sight – to construct an equation generally called kinetic equation for which the solution, i.e. Eq. (1), is already known. In the kinetic equation the coefficients involve  $S$  and  $\rho$ , i.e. the new problem is by no means less complex than the initial one (which is quite natural, though). However, the change to the binary version, classical centers-of-mass and other, more specific approximations is much more evident in these coefficients.

If  $n, m \dots$  are the quantum indices of the Hamiltonian of the active molecule, it appears that  $\kappa = \sum_{n, m} g_{nm}(\omega) M_{nm}$ , and the kinetic equation under discussion is of the form:

$$i(\omega - \omega_{nm}) g_{nm} + M_{nm} \rho_m^{(1)} = (\omega - \omega_{nm})^2 \Gamma_{nm} + I_{nm} \quad (2)$$

In Eq. (2)  $M_{nm}$  and  $\rho_m^{(1)}$  are the matrix elements of  $M$  and  $\rho^{(1)}$ , the latter being the Hibbs density matrix of the active molecule,  $\omega_{nm}$  is the line center corresponding to the transition  $m \rightarrow n$ , and  $\Gamma_{nm}$  and  $I_{nm}$  are the matrix elements of the operators:

$$\Gamma = \int_0^{\infty} dt (\exp(i\omega t)) (\text{Tr}_y C(t) \rho^{(2)} g C^{-1}(t))_{(av)} \Phi; \quad (3)$$

$$I = (1/i\hbar) \int_0^{\infty} dt (\exp(i\omega t)) (\text{Tr} C [\partial U / \partial t, \rho^{(2)}] g C^{-1})_{(av)} \Phi \quad (4)$$

Definitions (3) and (4) involve the operator  $g$  with the matrix elements  $g_{nm}$ , the Hibbs matrix of the "bath" molecule  $\rho^{(2)}$  ( $\text{Tr}_y$  is the trace operation over its variables),

and the solution of the  $\text{U}^{\text{U}}$ ding equation  $C$  for two colliding molecules with the Coulomb energy of the intermolecular interaction  $U$ . The classical motion of centers-of-mass is governed by the potential  $V$  mentioned earlier. The notation

$$(\dots)_{(av)} = N v \int dR R z(R) \int dt_0 \quad (5)$$

denotes averaging over collisions, where  $N$  is the number of bath molecules in the unit volume,  $v$  is the average velocity of the active molecule,  $t_0$  is the onset of the collision (i.e. it defines the initial conditions of the equation for  $C$ ), and  $\Phi$  is the average of  $D$  over a function describing statistical properties of the "drift".

The most essential thing is that the asymptotic cases of large and small frequency detunings  $\Delta\omega = |\omega - \omega_0|$  ( $\omega_0$  replaces here the line center frequency  $\omega_{nm}$ ) appear to be separated in the very equation (2). We need only Eq. (3) to describe the line periphery, and Eq. (4) to describe the line center. This fact is sure to considerably simplify the solution, because it enables one to resort to asymptotic methods in evaluating quantities (3) or (4) before solving Eq. (2).

A subsequent procedure for simplification of Eq. (3) begins with an asymptotic evaluation of the integral over  $t$ . In doing so, use can be made of the stationary phase method (which has been proved rigorously), and the equation for the stationary point can immediately be treated as a mathematical formulation of the energy conservation law. The favorable combination of mathematical and physical aspects is very symptomatic. The fact is that in similar cases an estimate of the type " $>$ " may be replaced by " $\approx$ ". Reducing dynamical problems to consideration of just one point offers a considerable scope for further simplifications.

First, there is no need to deal with the entire trajectory of the centers-of-mass at collision. It will suffice to consider a close vicinity of the stationary point and to approximate this part of the trajectory by a straight line. The Liouville theorem enables one to "transfer" averaging (5) to this very region. Second, the quantum problem reduces to the search for the eigenvalues of the operator  $H_1 + H_2 + U$  ( $H_{1,2}$  are the Hamiltonians of the active and bath molecules), and their parametric dependence on  $t$ . (The latter enters into  $U$  via the classical centers-of-mass). Third, a fairly simple formula of the type  $R = C' / \Delta \omega^a$ , where  $C$  and  $a$  are constants, is found to be appropriate for approximation of the intermolecular separation at a stationary point, and  $\text{Tr}_y \rho^{(2)}(\dots)$  gives, together with the other numerical values from Eq. (5), one more constant  $D'$ . These quantities are very slow functions of the frequency detuning.

The final formulas for the absorption coefficient  $\kappa_j$  on the periphery of the line centered at  $\omega_j$  with the intensity  $S_j$  take the form:

$$\kappa_j = S_j q_j F_j G_j \Phi_j;$$

$$q_j = (\omega / \omega_j) (1 - \exp(-\hbar \omega / k \Theta)) (1 - \exp(-\hbar \omega_j / k \Theta))^{-1};$$

$$G_j = D' C'^{3/a} (|\omega - \omega_j| + |\omega + \omega_j| \exp(\hbar \omega_j / k \Theta));$$

$$F_j = (1 / R_j) \int_0^{R_j} R (R_j^2 - R^2)^{-1/2} \exp(-V(R) / k \Theta) dR;$$

$$\Phi_j = \exp(-\omega^2 / c^2) d \tau_j.$$

The last-written expression is derived for the simplest "diffusion" model of the drift,  $d$  is numerically equal to the diffusion coefficient at a pressure of 1 atm, and  $\tau_j$  has the meaning of the relaxation time:

$$\tau_j = (2\pi N v \int_0^{R_j} dR R \exp(-V(R) / k \Theta))^{-1}, \quad R_j' = \alpha R_j$$

with one more constant  $\alpha$ . For an extended discussion of the constants see Refs. 3–11, 17, and 19.

We will not consider here specific applications because each of them would require a special and fairly detailed introduction. It is apparent, however, that a simple and reliable procedure for calculating the input quantity, i.e. the light absorption coefficient, should form the basis of these applications. These characteristics are predetermined by a clear and comprehensive physical picture of the line periphery.

The subsequent sections should be regarded as an illustration of general concepts. A list of similar examples can be made indefinitely long, and the cases discussed here are not anything unique. In the monographs and papers cited above the reader may find descriptions of other bands of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  and spectra of other gases. We can state that all the available experimental data on the light absorption and emission in the band and line wings (i.e. in the troughs between strong lines of a band) have been interpreted quantitatively.

## 2. SPECTRAL REGION FROM 8 TO 12 $\mu\text{m}$

Basic properties of the major atmospheric window,  $\kappa = a p P + b p^2$  ( $a = a(\omega)$ ,  $b = b(\omega)$ ), where  $p$  and  $P$  are the partial pressure of the water vapor and the total gas pressure,  $b p^2 > a p P$  even though  $P > p$ ;  $d \kappa / d \Theta > 0$  for atmospheric temperatures, have been long studied experimentally in considerable detail and are of necessity cited in the literature.

It should be added that  $d \kappa / d \Theta$  changes sign as  $\Theta$  is further increased (see Fig. 2). The calculations using LARA software package developed at the Institute of Atmospheric Optics (IAO SB RAS) have shown that the problem should most probably be regarded by taking into account the weak lines with Lorentzian shape in the spectral region of interest.

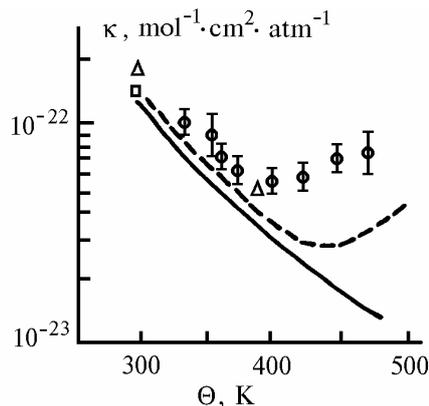


FIG. 2. The light absorption in the atmospheric windows. Plotted on the ordinate is  $b p^2$ , the dominant part of  $\kappa$  for frequency of  $1200 \text{ cm}^{-1}$ . Experimental data  $\circ$  and  $\Delta$  are taken from Ref. 32 and  $\square$  – from Ref. 33. Solid line depicts the calculations using the approximate formula from Ref. 33, and the dashed line refers to the calculations cited in this paper.

Methodically, the notable feature of the problem is that the known hypotheses on the origin of the continuum listed in the first column of Table I are indistinguishable in consequences from each other when the foregoing relationships are discussed. For example, in all versions there appears the same factor  $\exp(\eta / \Theta)$  that describes the temperature dependence. In doing so, the meaning of the constant  $\eta$  is different (see Table I). However, the numerical values of these constants are roughly the same (needless to say that this fact can be properly accounted for), and it is impossible to decide between the potential candidates. The rest of the relationships are also readily interpreted within the framework of any hypothesis.

TABLE I.

Hypothesis for the origin of continuum and the relevant reference	The meaning of $\eta$
Rotational band wings of water vapor <sup>34</sup>	Potential well depth
H <sub>2</sub> O dimers <sup>35</sup>	Binding energy
Aerosol <sup>36</sup>	Evaporation heat per a molecule
Ionic clusters <sup>37</sup>	—”—

Note that a suggestion was made that the continuum be treated as a quantum optics effect.<sup>38</sup> However, criticism of that approach is beyond the scope of the present paper.

A way out of what might seem to be the impasse (the problem will not be solved in terms of universal constants, will it?) is in fact fairly obvious. The ideas under discussion should be extended to include related areas (light emission, nonlinear optics, etc.). This time, however, the implications would be radically different and direct experiments would completely solve the problem.

The practical and scientific importance of the atmospheric window problem has been discussed time and again by Academician V.E. Zuev (see Refs. 1, 8–10 and the monograph<sup>11</sup> by Professor V.V. Fomin, one of his disciples) who made a remarkable contribution to the development of a constructive approach to its solution. As a matter of fact, it has been formulated in the preceding paragraph and the results of its realization are generally outlined below.

Let us begin with a problem on the emission coefficient  $\chi$  appearing in the transfer equation. A conventional treatment of self–radiation of the medium as quantum fluctuations of the equilibrium dipole moment within semiclassical electrodynamics, the fluctuation–dissipation theorem known from statistical physics, and the Maxwell equations including fluctuations like the Langevin process hold that the necessary and sufficient condition for the local thermodynamic equilibrium (i.e. the relation  $\chi = B \kappa$  where  $B$  is the Planck function) implies no spatial dispersion in  $\text{Im } \epsilon$ . As indicated in Section 1, it is the picture of the line periphery that may be a conceivable reason for this kind of dispersion, which is why the local thermodynamic equilibrium in band wings must be disturbed. There is a reliable experimental verification of this prognosis,<sup>12,13</sup> and it is in effect apparent that other assumptions for the nature of continuum fail to account for the fact being discussed.

Another argument of comparable significance is concerned with nonlinear spectroscopy. The pertinent experimental program was performed at IAO SB RAS.<sup>14–16</sup> In Section 1 we have discussed the role of the classical potential of intermolecular interaction. According to the quantum–mechanical laws  $V$  is the binary Coulomb energy averaged over the density matrix  $\rho$  of intramolecular variables. In a strong laser field  $\rho$  depends on the field intensity  $I$  and the above–mentioned “causal chain” leads to the nonlinear effect, i.e. to the  $I$ –dependence of  $\kappa$ . Particularly remarkable is the fact that nonlinear spectroscopy normally deals with resonant processes associated with isolated lines (systems with a small number of levels found in nonlinear optics). In the situation discussed, on the contrary, the large frequency detuning requirement is as indispensable as that of the band wing where the sum of a large number of lines (in

this regard the effect is cooperative) enhances weak nonlinear nonresonant interactions on quantum transitions.

The experimental data have exhibited an isotopic feature of the nonlinear effect that  $\kappa(I)$  for H<sub>2</sub>O and D<sub>2</sub>O is different while the linear absorption for the two isotopes is the same. Another fact of interest is that the field dependence of the relaxation time in the resonance case is in complete contrast to that found in the nonresonance case. Both results are explained quite naturally by theory of the line periphery.

### 3. THE 4.3 $\mu\text{m}$ CO<sub>2</sub> BAND WING

The possibilities of the line wing theory for a quantitative interpretation of the experimental data on the 4.3  $\mu\text{m}$  CO<sub>2</sub> band wings were repeatedly demonstrated. One of its practical applications is a time–saving computational procedure for the absorption coefficient and absorption function within the CO<sub>2</sub> spectral bands,<sup>17</sup> which ensures the “experimental” accuracy (i.e. the error does not exceed the measurement error). As an illustration of qualitative potentialities of the theory mention can be made of double intersections of spectral curves taken at different temperatures and the parity between the limits of the piecewise approximation from Ref. 18 and those of so–called multipole dispersion naturally resulting from the theory per se, etc.

Of certain practical interest is the identification of spectral “points” where the absorption coefficient is essentially independent of temperature. Clearly, these frequencies are important for the problem of atmospheric sensing, for one of the unknowns can be eliminated by choosing appropriate frequencies. A convincing example of evaluation of the total CO<sub>2</sub> content from measurements of the vertical transmittance is given in Ref. 19.

An interesting corollary to the theory is a possibility to solve an inverse problem of retrieving the classical intermolecular interaction potential from empirical data on the absorption coefficient in the band wings. Four substantive issues are involved in this case. First, the potential is identical to the one used in calculations of the thermodynamical quantities. Second, its analytical form need not be specified beforehand, as distinct from other methods. Third, the line wing data provide information on the behavior of  $V$  at small intermolecular separations. Fourth, the measurements at different  $\Theta$  enable one to construct  $V(\Theta)$ . The very existence of the latter dependence follows from the definition of  $V$  in quantum mechanics (see Section 1), for  $\rho$  depends on  $\Theta$  (see Ref. 20).

TABLE II.

$\omega$ , cm <sup>-1</sup>	Experimental $\kappa$ , cm <sup>-1</sup> ·amagat <sup>-2</sup>	Calculated $\kappa$
2410	0.00353	0.00326
2420	0.00182	0.00180
2430	0.00105	0.00106
2440	0.000683	0.000693
2450	0.000464	0.000474
2460	0.000310	0.000311
2470	0.000181	0.000182
2480		0.000130

Note: the experimental and calculated data are given for  $\Theta = 920$  K.

Figure 3 and Table II are given as an illustration of the subject under discussion. The temperature dependent

parameters  $\epsilon$  and  $\sigma$  of the Lennard–Jones potential  $V(R) = 4\epsilon((\sigma/R)^{12} - (\sigma/R)^6)$  for the pair  $\text{CO}_2 - \text{CO}_2$  were inferred from empirical data up to  $\Theta = 700$  K. The temperature dependence of  $\epsilon$  and  $\sigma$  was extrapolated to  $\Theta = 10^3$  K. The results of comparison of the calculated absorption coefficient using this potential and the corresponding experimental data (see Table II) show an excellent agreement. We can say with reasonable confidence that exact calculation is guaranteed of the temperature dependence of the absorption coefficient at frequencies used for inversion of the satellite–based data on the outgoing radiation.

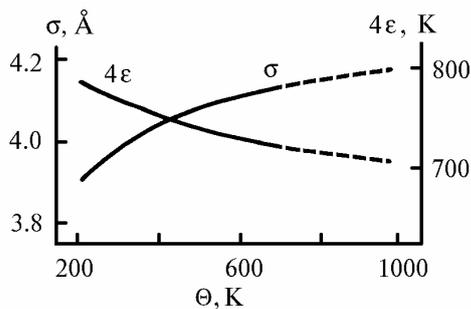


FIG. 3. Temperature dependence of parameters of the Lennard–Jones potential. Solid curves depict  $\epsilon$  and  $\sigma$  as solution of the inverse problem based on the experimental data from Ref. 33. Dashed curves show extrapolation.

#### 4. NON–LTE IN THE UPPER ATMOSPHERE

Let us consider at this point an example of implications of the fairly general aspects of the line wind theory that came to be comprehensible when discussing the line periphery. We meant the behavior of the emission coefficient in the upper atmosphere. In Section 2 mention has already been made of the relationship between disturbance of the local thermodynamic equilibrium (non–LTE) and the spatial dispersion of the imaginary part of the dielectric constant. At a low gas density the general factors responsible for the dispersion are quite obvious. These are a long free path as compared to the wavelength and the effect of collisions on the Doppler line shape. To the above circumstances must be added the factors leading to a deviation of the density matrix from the standard Hibbs form, viz fluctuations of the distribution function of the centers–of–mass and the chemical reactions involved. The latter are of special importance for passive sounding of the upper atmosphere (e.g. limb measurements from satellite–borne platforms).

The relevant formulas are listed in Ref. 21. Here it is worth considering a pure qualitative aspect but again associated with the very nature of the non–LTE in the upper atmosphere.

The standard treatment of the problem pioneered in Ref. 22 and detailed in Refs. 23 and 24 proceeds from the postulate that occasional collisions found at low gas pressures fail to reestablish the equilibrium distribution of vibrational (and electronic) states. At times (see, for example, Ref. 25) this point of view is expressed in a straightforward manner: "another" vibrational temperature is introduced into the density matrix and this new temperature is to be found from the solution of the inverse problem. A "balance" scheme produces a means for translating this *a priori* assumption into mathematical terms. It implies that intramolecular transitions induced

by interactions with the field or by intermolecular collisions are assumed to be identical (in terms of "collisions"), additive and independent of each other when counting the events of arrival at or escape from an energy level. In doing so, one cannot but mention a procedure used in writing the transfer equation wherein use is made of the Einstein coefficients. All this would seem to impart a due solidity to the whole concept. However, nothing of the kind happens, as it is at this point where a subtle trap is hidden.

Indeed, the use of the Einstein coefficients is undoubtedly an unexceptionable expedient when the equilibrium situation is discussed (for example, radiation in a cavity with absolutely black walls). It is in this very case where, according to the rules of quantum electrodynamics,<sup>26</sup> the "photon-particles" analogy is valid, since knowledge of the field energy will suffice for a complete description of the situation. It should be remembered that the photon wave functions are defined in the space which is the Fourier–transform of a real space,<sup>26,27</sup> and the validity of reference to the "photon-particle" analogy (and consequently the legitimacy for collisions between two molecules and those between a molecule and a photon to be treated identically) should be proved separately. This pertains equally to the concept of the "photon density" which is a must when writing the transfer equation is such a manner. However, this equation is intended for a description of the light propagation which is rather a nonequilibrium process, in the sense that use should be made of travelling waves rather than standing waves that are associated with the equilibrium of the very field itself. (As is the case, for example, with a closed cavity with no energy transfer. The vanishing of the Poynting vector is the governing feature of standing waves).

The fundamental consequence of this view on the problem is that the emission coefficient appears to be a function of intensity (!?). Such a situation according to the rules of modern statistical semiclassical electrodynamics is to be encountered only in the case of a strong laser field (see discussion of this problem, for example, in Ref. 28). It has long been realized (for example, in the problem of the line shape) that, when solving any specific problem of the interaction between a molecule and a field, it is the effect of collisions on this interaction that must be examined. (Some qualitative aspects have been mentioned in Sec. 1). The calculations are performed in the framework of the equation for the density matrix (or the Schrödinger equation) wherein, naturally, the field and the collisions are by no means independent or equal in their rights. The use of a similar procedure (which, incidentally, is common in laser physics,<sup>28</sup> nonlinear spectroscopy<sup>9</sup> and plasma physics<sup>30</sup>) does result in a combination of the Maxwell equations, Schrödinger equation and the fluctuation-dissipation theorem with the consequences for the emission coefficient discussed earlier in this section.

For the spatial dispersion of the type discussed in Sec. 1 the relations for  $\kappa$  and  $\chi$  have the form:

$$\kappa = (4 \pi \omega / c) \operatorname{Im} \Gamma(\omega, \lambda) \Big|_{\lambda=(\omega/c)} ;$$

$$\chi = (4 \hbar \omega^5 / \pi^2 c^4) \int_0^\infty \frac{d\lambda \lambda^2 \operatorname{Im} \Gamma(\omega, \lambda) \Lambda(\omega, \lambda)}{|\lambda^2 - \omega^2 / c^2 - (4 \pi \omega^2 / c^2) \Gamma(\omega, \lambda)|^2} ,$$

where  $\Gamma$  is the Fourier transform of  $f$  over  $r$ ,

$$\Lambda = \sum_{n,m} \frac{\rho_n^{(1)} + \rho_m^{(1)}}{\rho_n^{(1)} - \rho_m^{(1)}} \Gamma_{nm},$$

and  $\Gamma_{nm}$  appear upon representation of  $\kappa$  as a sum over the spectral lines (if  $Tr$  in Eq. 1 is written explicitly). The last expression is a general formulation of the fluctuation-dissipation theorem in the case where the density matrix is different from the Hibbs form (owing to, say, the chemical reactions), otherwise we have:

$$\Lambda = \frac{1 + \exp(-\hbar\omega / \kappa\Theta)}{1 - \exp(-\hbar\omega / \kappa\Theta)} \Gamma.$$

Worthy of mention is yet another interesting physical problem pertaining to the construction of the distribution function  $W(\mathbf{r}, t, \mathbf{v})$  for the centres-of-mass  $\mathbf{r}$  and their velocities  $\mathbf{v}$  ( $t$  is the time), which, as a matter of fact, provides a description of the spatial dispersion of  $\text{Im } \epsilon$  for low gas densities. The formulation of such a physical kinetics problem is also due to the physical picture of the line shape. It is precisely here that an answer is hidden to the question: whether the use of the Voigt contour alone in the calculations relating to the upper atmosphere is justified, inasmuch as the Voigt contour ignores the effect of collisions on the Doppler line shape, which appears to be an essential factor. Incidentally, it is to be noted that an extensive body of experimental evidence of this effect was produced at IAO SB RAS,<sup>31</sup> with the development of the relevant experimental techniques being initiated by Academician V.E. Zuev.

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