ON ABSORPTION AND EMISSION OF LIGHT IN THE UPPER ATMOSPHERE

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The processes of molecular emission and absorption of light in the upper layers of the atmosphere are discussed within the framework of modern semiclassical statistical electrodynamics.

1. INTRODUCTION

The equation of radiative transfer through a molecular medium

$$\mathbf{k}_0 \mathrm{grad}\, J = -\kappa J + \eta \tag{1}$$

for the spectral intensity J of a beam at the frequency ω propagating along the direction of a unit vector $\mathbf{k}_0$ includes $\kappa(\omega)$ and $\eta(\omega)$, i.e., the absorption and emission coefficients. If

$$\eta = B(\omega, \mathrm{H})\kappa , \tag{2}$$

where B is the Planck function, Θ is the temperature we have the so–called local thermodynamic equilibrium.

This paper concerns with the problem of κ, η, and Eq. (2) for the upper atmosphere. This analysis will remain unchanged if the light scattering is to be taken into account in Eq. (1).

In Sec. 2 the derivation of Eq. (1) using the semiclassical statistical electrodynamics is reminded. A criticism of a widely recognized opinion about the cause of Eq. (2) violation in the upper atmosphere is given in Sec. 3. The peculiarities inherent in κ and η at small pressures are discussed in Secs. 4 and 5. Some conclusions are drawn in Sec. 6.

The paper is written as a methodological (and to some extent authorized) review. Its aim is to attract attention to those aspects of the problem which differ the approach based on Maxwell's equations from the phenomenological one based on the "photon analogies". The question appears to be nontrivial when the radiative processes in the upper atmosphere are treated.

2. SEMICLASSICAL STATISTICAL ELECTRODYNAMICS AND THE EMISSION COEFFICIENT

Within the "optical version" (nonmagnetic dielectric) Maxwell's equations (for the electric field strength $\mathbf{E}(\mathbf{r}, t)$ at a point $\mathbf{r}$ and at time t)

$$\mathrm{rot\,rot}\,\mathbf{E}(\mathbf{r}, t) + \frac{1}{c^2}\frac{\partial^2 \mathbf{E}}{\partial t^2} + \frac{4\pi}{c^2}\frac{\partial^2 \mathbf{P}}{\partial t^2} = 0 \tag{3}$$

involves the dipole moment of a unit volume $\mathbf{P}(\mathbf{r}, t)$ and c is the speed of light. For reasons that will become clear in Sec. 4 it is worthwhile to study a medium with a spatial dispersion when the spectral component is

$$\mathbf{P}(\mathbf{r}, \omega) \equiv \frac{1}{2\pi}\int\limits_{-\infty}^{\infty} \mathbf{P}(\mathbf{r}, t)\, \mathrm{e}^{ixt}\, \mathrm{d}t = \int f(\omega, \mathbf{r}')\, \mathbf{E}(\mathbf{r} - \mathbf{r}', \omega)\, \mathrm{d}\mathbf{r}' \tag{4}$$

with some function $f(\omega, \mathbf{r}')$; $\mathbf{E}(\mathbf{r}, \omega)$ is the spectral component of $\mathbf{E}(\mathbf{r}, t)$. The relations

$$\mathbf{P}(\mathbf{r}, \omega) = \frac{\varepsilon(\omega) - 1}{4\pi}\mathbf{E}(\mathbf{r}, \omega) , \; f(\omega, \mathbf{r}') \sim \delta(\mathbf{r}') \tag{5}$$

demonstrate the passage from Eq. (4) to the conventional version with the dielectric constant $\varepsilon(\omega)$.

In the phenomenological electrodynamics the function f (or the quantity ε) is announced to be an empirical value.[1,2] The term "semiclassical electrodynamics" appears when the quantum mechanics is used for calculation of f (see, for example, Refs. 3–9), i.e.,

$$\mathbf{P}(\mathbf{r}, t) = \mathrm{Tr}\, \hat{\rho}(t)\, \hat{\mathbf{P}}(\mathbf{r}) , \quad i\hbar\frac{\partial\hat{\rho}}{\partial t} = \hat{H}\hat{\rho} - \hat{\rho}\hat{H} ,$$

$$\hat{H} = \hat{H}_0 + \hat{H}_{0R} , \quad \hat{H}_{0R} = -\sum_{\alpha} e_\alpha \mathbf{r}_\alpha \mathbf{E}(\mathbf{r}_\alpha, t) , \tag{6}$$

$$\hat{\mathbf{P}}(\mathbf{r}) = \sum_{\alpha} e_\alpha \mathbf{r}_\alpha \delta(\mathbf{r} - \mathbf{r}_\alpha) .$$

In Eqs. (6) $\hat{\rho}$ is the density matrix of a system which is described by the Hamiltonian $\hat{H}_0$ before the field switching, $\hat{\mathbf{P}}$ is the dipole moment operator of a unit volume, and the Hamiltonian $\hat{H}_{0\mathrm{R}}$ that represents the energy of interaction between the system and the field, in the dipole approximation, includes the charges e_α of the particle α. The particle coordinate $\mathbf{r}_\alpha$ is naturally considered to be the argument of the wave function. The first and the second relations of Eqs. (6) are common definition of a quantum average and the problem of a quantum system evolution in the electromagnetic field which is equivalent to the Schrödinger equation.

The adjective "statistical" implies here the treatment of the spontaneous radiation as fluctuations of the equilibrium dipole moment. A detailed discussion of similar statement can be found in Refs. 1, 7–14, and, naturally, the quantum fluctuations' problem itself is a part of the quantum theory philosophy (see, for example, Ref. 15). The corresponding correlator in terms of Eqs. (6) has the form

$$\Pi_x = \mathrm{Tr}\, \hat{\rho}\, \frac{1}{2}\left(\hat{x}\hat{x}'(t) + \hat{x}'(t)\hat{x}\right) . \tag{7}$$

In Eq. (7) $\hat{x}$ denotes the operator of some physical quantity and $\hat{x}'(t) = \exp(-t/i\hbar)\hat{H}_0\, \hat{x}\, \exp(t/i\hbar)\hat{H}_0$. The equilibrium situation is normally talked about if in Eq. (7) we have

$$\hat{\rho} \to \hat{\rho}^{(0)} \tag{8}$$

and $\hat{\rho}^{(0)}$ is the density matrix of the quantum system before switching on the field. In fact, Eq. (8) is the initial condition for Eq. (6), which is quite sufficient for calculating quantity (7), since the parameter of a series expansion over powers of the field[5,6] (D is the matrix element of the dipole moment) is

$$\xi = DE/(\hbar\beta) \ll 1. \tag{9}$$

Actually, under conditions of the upper atmosphere β is either the Doppler linewidth γ_D or $\sqrt{\gamma_D\gamma_L}$, where γ_L is the dispersion linewidth. For solar radiation the value E hardly reaches 10 W/cm.

Simple qualitative considerations readily allow one to represent spontaneous radiation as a result of irregular motion of the dipole moment around its zeroth (in the absence of the field) mean (see Eq. (8)). The foregoing is also obvious from the formal point of view, i.e., the fluctuations $\delta\mathbf{P}(\mathbf{r}, t)$ should be added to $\mathbf{P}$, and the replacement of $\mathbf{P} + \delta\mathbf{P}$ for $\mathbf{P}$ in Eq. (3) makes it be an nonhomogeneous equation. A particular solution of the latter equation ($\sim \delta\mathbf{P}$) will just describe self–emission of a medium. To obtain Eq. (1) it is sufficient to use the energy conservation law in electrodynamics following from Eq. (3), to assume J to be the Poynting vector and to introduce the rays of geometrical optics. (The latter is undoubtly valid for the medium without light scattering). To this end taking into account Eq. (4) one obtains[14]

$$\eta = \frac{4\hbar\omega^5}{\pi^2 c^4} \int\limits_0^\infty \frac{d\lambda\lambda^2 \operatorname{Im} \Gamma(\omega, \lambda)\, \Lambda(\omega, \lambda)}{\left| \lambda^2 - \frac{\omega^2}{c^2} - \frac{4\pi\omega^2}{c^2}\Gamma(\omega, \lambda) \right|^2}, \tag{10}$$

$$\kappa(\omega) = \frac{4\pi\omega}{c} \operatorname{Im} \Gamma(\omega, \lambda) \Big|_{\lambda = \omega/c}. \tag{11}$$

The function $\Gamma(\omega, \lambda)$ is the Fourier transform over $\mathbf{r}$ of the function f from Eq. (4), $\Lambda(\omega, \lambda)$ is the spatiotemporal spectrum of correlator (7) for $\delta\mathbf{P}$. The quantities Γ and Λ depend on $\lambda = |\lambda|$ in the case of an isotropic medium.

The problem on Λ is solved with the aid of the fluctuation–dissipation theorem and now we shall only schematically remind its derivation.[10–12, 16, 17]

Let a volume with a sufficiently large number of molecules be assumed "the system" in Eqs. (6). The solution of Eqs. (6) to the first order of the perturbation theory (unlike Eqs. (7) and (8) to the zeroth order $\mathbf{P} = 0$) with respect to parameter (9) is well known from the textbooks on quantum mechanics (see, for example, Ref. 18). In this case we obtain for Γ the expression $\Gamma(\omega) \sim \sum\limits_{a,b} |\alpha_{ab}|^2\, \delta(\omega - \omega_{ba})(\rho_a^{(0)} - \rho_b^{(0)}) \equiv \sum\limits_{a,b} \Gamma_{ab}(\omega)$. Here a, $|a>$, and E_a are the quantum indices, eigen functions and eigenvalues of $\hat{H}_0$; $\omega_{ba} = (E_b - E_a)/\hbar$, $\rho_a^{(0)} = <a|\hat{\rho}^{(0)}|a>$ is the probability of the equilibrium state a (before switching on the field), $x_{ab} = <a|\hat{x}|b>$ and $\hat{x}$ is the vector component of $\hat{\mathbf{P}}$. The δ–function is the mathematical consequence of the "golden" Fermi rule, and singularity is removed because $\sum\limits_{a,b}$ is practically an integral if the number of molecules is large.

The same technical procedures give for spectrum (7) the quantity $\sim \sum\limits_{a,b} |\alpha_{ab}|^2 \cdot \delta(\omega - \omega_{ba})(\rho_a^{(0)} + \rho_b^{(0)})$. Now it can readily be shown that

$$\Lambda = \sum_{a,\, b} \frac{\rho_a + \rho_b}{\rho_a - \rho_b} \Gamma_{ab}(\omega) \tag{12}$$

which is just the general formulation of the fluctuation–dissipation theorem.[12] There is no problem to find the coefficients in the latter relations, they are taken into account in Eqs. (10) and (11) and are chosen to fit the equality in Eq. (12).

In the case of thermodynamic equilibrium (or local equilibrium in the sense of Ref. 16), when

$$\rho^{(0)} = \frac{1}{Z} \exp(-\hat{H}_0/k\Theta), \tag{13}$$

where k is the Boltzmann constant, Z is the normalization factor obtained from the condition $\operatorname{Tr} \rho^{(0)} = 1$, the δ–function in Γ_{ab} gives a possibility of rewriting Eq. (12) in the form

$$\Lambda = \frac{1 + \exp(-\hbar\omega/k\Theta)}{1 - \exp(-\hbar\omega/k\Theta)} \Gamma(\omega, \lambda), \tag{14}$$

and in fact Eq. (14) is the most commonly used formulation of the theorem. Relations (14) and (11) show that it is sufficient for calculating the correlator of quantum fluctuations to have any information about the absorption coefficient, for example, empirical calculated in the binar approach, etc.

ON THE BREAKING EQ. (2) IN THE UPPER ATMOSPHERE. A CRITICAL REVIEW

There exists an opinion, when calculating η for the upper layers of the atmosphere, which comes evidently from Ref. 19 (see also Ref. 20) that relation (13) is not fulfilled under these conditions because rather rare collisions are unable to restore the equilibrium destroyed by radiation. It is *a priori* taken that just the vibrational (and electronic) states cannot relax to the state described by Eq. (13). A formal result of such an approach is the following expression:

$$\eta = \kappa B \frac{\tau' + \tau y}{\tau' + \tau}, \quad y = \frac{\int J(\omega, \mathbf{k}_0)\, d\omega\, d\mathbf{k}_0}{4\pi \int k(\omega)\, B(\omega)\, d\omega}, \tag{15}$$

where τ is named the vibrational collisional relaxation time and τ' is the lifetime of a molecule in an excited state. It is understandable that as $\tau \to 0$ Eq. (15) takes the form of Eq. (2) that corresponds to the low layers of the atmosphere.

The same concepts in a more refined mathematical performance were presented in Ref. 21 and the results were used for extensive calculations of the intensity.[22–24] In Refs. 25 and 26 it was simply accepted that the vibrational temperature Θ' (in the sense of Eq. (13)) differs from Θ and the inverse problem was solved for Θ'.

The papers now discussed are based on the "balance approach" implying that the transitions between molecular states due to the interaction with the field and intermolecular collisions are considered as independent. Therefore the change of the population of the state with time can be evaluated as the difference between the number of acts of coming to and from the corresponding energy level. Similar approach to description of the processes under study existed in the beginning of the "laser revolution" (see, for example, Ref. 27) and is very popular in astrophysics (Refs. 28 and 29). However, beginning from Refs. 3, 4, and 9 the "wave" point of view (based on Eqs. (3) and (6)) has been accepted as a common one. In fact, derivation of Eqs. (1), (10) and (13) from (3) and (4) is its technical realization. Note, in addition, that modern nonlinear spectroscopy, which pays great attention to the effects occurring under low gas pressure (see, e.g., Refs. 30 and 31), as well as plasma physics (see, Refs. 17, 32–34) are entirely based on semiclassical electrodynamics.

The main statement of the present critical review is that the balance approach fails in application to a rather delicate problem of breaking relation (2).

Discussion of this problem seems to be quite necessary. Actually, Eq. (15) shows that η depends on J. This, in turn, drastically changes the mathematical structure of Eq. (1), i.e., in addition to an ordinary nonhomogeneous differential equation one has to solve the integral equation relative to y from Eq. (15). Moreover, there arise the ideas of the lasing effect in the upper atmosphere (see, for example, Ref. 35). Meanwhile, the discussion of Eqs. (7)–(9) and (10)–(12) shows unambiguously that the relationship between η and J can only exist for strong laser fields (spontaneous emission in the presence of a strong field[8,36,37]) independently of the fact is Eq. (13) valid or not. To say generally, we have just formulated the main argument in the spirit of *reductio ad absurdum*. Of course, this does not make the analysis of considerations leading to Eq. (15) unnecessary.

Necessary element of the balance scheme is the use of considerations based on the Einstein coefficients for the derivation of Eq. (1) itself. This procedure is quite relevant in the case of equilibrium emission. Really, it is quite sufficient to know the energy of the system in order to analyze such an emission and according to quantum electrodynamics[38] the photons–particle analogy should work here. (Remind that the photon wave functions exist in space, which is a Fourier transform of the real world[38–39]). Just for these reasons we can operate with a concept of "the photon density" as with a "real particle density" treating the molecule–to–molecule and molecule–to–photon collisions as the events of the same kind. However, Eq. (1) concerns the propagation of light (not the field properties in a cavity with absolutely black walls) and therefore the efficiency of the "photon–particle" analogy should be proved. But it is accepted without additional considerations and, moreover, it is supplemented with new elements (further we discuss Ref. 19). The *a priori* statement nonequilibrium behavior of the vibrational states yields the expression $\eta = \kappa B(E/E^{(0)})$, where E and $E^{(0)}$ are the mean energies (in a statistical sense) of vibrational states when thermodynamic equilibrium is violated and when it takes place, respectively. After that Curtis and Goody[19] write down the equation $\mathrm{d}E/\mathrm{d}t = (-\gamma)(E - E^{(0)})$ with the vibrational relaxation time $\tau = 1/\gamma$. It could seem that for calculation of the ratio $E/E^{(0)}$ entering into η it is necessary to find the $\lim E/E^{(0)}$ as $t \to \infty$, i.e., a natural stationary limit, but then $E/E^{(0)} = 1$ that certainly does not suit the authors of Ref. 19. Therefore, there appears a trick, namely, based on almost semantic sense of the quantities J and $\mathrm{d}E/\mathrm{d}t$ the equality is written

$$-\gamma(E - E^{(0)}) = \int (\mathbf{k}_0 \operatorname{grad} J)\, \mathrm{d}\omega\, \mathrm{d}\mathbf{k}_0 \,. \tag{16}$$

After substitution of Eq. (1) and the above–obtained η into Eq. (16) the equation for $E/E^{(0)}$ appears that yields Eq. (15). (The quantity τ' is announced to be the value of $\sim \int \kappa(\omega)\, B(\omega)\, \mathrm{d}\omega$ what quite well agrees with quantum mechanics.[18])

The comment of similar considerations should be based on the well–understood relations between the process of quantum system interaction with field and their relaxation. The central statement of the considerations is that both these factors should be taken into account simultaneously since they interfere in the same quantum problem (6). An excellent qualitative illustration of the resonance case with $\omega = \omega_0$, where ω_0 is the frequency of the molecular transition can be found in a comprehensive analysis in Ref. 40. (For the line wing the situation is even more definite.[4,41,42]) On a free path the wave function of the molecule interacting with the field oscillates (with the frequency $\mathbf{ED}/\hbar$, see Eq. (9)) between the upper and the lower states.[43] The collision is necessary to interrupt this periodical process and only then absorption of a quantum could take place. Of course, it is also possible to calculate the transition probability per unit time using periodic wave functions. It will contain $\delta(\omega - \omega_0)$ (see, for example, Ref. 18). Actually, the singularity is removed by substitution of the line contour instead of δ–function, but for its appearance the relaxation taking part in the game simultaneously with the field is absolutely necessary condition.

As the formal illustration of these "wave" concepts the popular now "laser" system of equations can be considered as obtained from Eqs. (6) making use the reduction to the density matrix of an "active" (interacting with the field) molecule. For, example, for a two–level system it can be written as[8]

$$\partial\rho_{nn}(t)/\partial t + \upsilon \operatorname{grad}_{\mathbf{R}} \rho_{nn} = \frac{1}{i\hbar}(\rho_{nm}\mathbf{D}_{mn} - \mathbf{D}_{nm}\, \rho_{mn})\mathbf{E} - \gamma_n(\rho_{nn} - \rho_n^{(0)}),$$

$$\partial\rho_{mm}(t)/\partial t + \upsilon \operatorname{grad}_{\mathbf{R}} \rho_{mm} = -\frac{1}{i\hbar}(\rho_{nm}\mathbf{D}_{mn} - \mathbf{D}_{nm}\, \rho_{mn})\mathbf{E} -$$

$$-\gamma_m(\rho_{mm} - \rho_m^{(0)}) \,,$$

$$(\partial/\partial t + \upsilon \operatorname{grad}_{\mathbf{R}} + i\omega_0 + \gamma_{nm})\rho_{nm} = \frac{1}{i\hbar}\mathbf{D}_{nm}(\rho_{nn} - \rho_{mm})\mathbf{E} \,,$$

$$\rho_{mn} = \rho_{nm}^{*} \,. \tag{17}$$

Now $\hat{\rho}$ is the density matrix of an active molecule, and its Hamiltonian $\hat{H}_0$ enters into Eq. (13). The values n, $|n>$, and E_n are the quantum index the eigenfunction and the eigenvalue of the operator $\hat{H}_0$, $\omega_0 = (E_n - E_m)/\hbar$, $\rho_{nm} = <n|\hat{\rho}|m>$, $\rho_n^{(0)} = <n|\hat{\rho}^{(0)}|n>$. For the dipole moment $\mathbf{D}$ of a molecule we have $\mathbf{D}_{nm} = <n|\mathbf{D}|m>$. Further, $\mathbf{R}$ and $\mathbf{v}$ are the coordinate of the molecular center of mass and its velocity. In a linear with respect to the field variant the term $\mathbf{v}\,\mathrm{grad}_{\mathbf{R}}(\,\dots\,)$ can be neglected, if compensated for this by introducing the Doppler effect according to the scheme discussed in Sec. 4. The numbers γ_n, γ_m, $\gamma_{nm} = \frac{1}{2}(\gamma_n + \gamma_m)$ are just the relaxation constants. As usual, $1/\gamma_n$ is the relaxation time. System (16) has to be examined together with Eq. (3) and with the obvious definition of the dipole moment $\mathbf{P} = N\int \mathrm{d}\mathbf{v} \sum (\rho_{nm}\mathbf{D}_{mn} + \rho_{mn}\mathbf{D}_{nm})$ (N is the number of active molecules in a unit volume).

Now the quantities entering into Eq. (16) can also be seen in Eq. (17). Actually, by writing an obvious relation $E = \sum (\rho_{nn}E_n + \rho_{mm}E_m)$ and by changing γ_n and γ_m for the average γ, as it is often made, one obtains

$$\frac{\gamma}{\tilde{\omega}}\int \kappa(\omega)\, J(\omega, \mathbf{k}_0)\, \mathrm{d}\omega\, \mathrm{d}\mathbf{k}_0 = \Delta E + 4\pi \int \eta\, \mathrm{d}\omega -$$

$$-\int \mathrm{d}\omega\, \mathrm{d}\mathbf{k}_0\, \mathbf{k}_0\, \mathrm{grad}\, J - \gamma(E - E^{(0)})\ . \tag{18}$$

In Eq. (18) ΔE is the change of the internal energy per unit time, ω is the average frequency, a stationary E is being implied here. Equation (18) is obtained by making use of quite common calculations including averaging over time, a passage to the spectral components and using the rules of Fourier transforms of the stationary functions. In the process of calculations a combination appears $\mathbf{E}(\partial\mathbf{P}/\partial t) = \mathbf{Ej} = Q$, where Q is the amount of the absorbed heat with $\mathbf{j} = \partial\mathbf{P}/\partial t$ being the current of coupled particles. Then for the spectral components we have $Q = \kappa J$ and Eq. (1) is taken into account.

By taking the assumption of Eq. (16) we obtain

$$\frac{\gamma}{\tilde{\omega}}\int \kappa(\omega)\, J(\omega, \mathbf{k}_0)\, \mathrm{d}\omega\, \mathrm{d}\mathbf{k}_0 = \Delta E + 4\pi \int \eta(\omega)\, \mathrm{d}\omega\ . \tag{19}$$

In the balance scheme extrapolated to the problem of light propagation the right–hand side of Eq. (19) should exactly coincide, for the stationary case, with the amount of disappeared energy of the field. However, it is possible only under the obviously absurd condition that $\gamma = \tilde{\omega}$ (?!).

In fact, the "wave" interpretation of Eq. (18) is quite evident, namely, it is the energy conservation law from the semiclassical electrodynamics. Equation (18) corresponding to the specific situations (17) does not have any special pragmatic meaning, and has been discussed here only for the sake of Eq. (19) which has to underline the arbitrariness of the assumption of Eq. (16).

4. ON THE ABSORPTION LINE SHAPE UNDER CONDITIONS OF THE UPPER ATMOSPHERE

Physical aspects of the problem on a spectral line shape under small pressures are well known, i.e., the Doppler effect has to be of a major importance.[44] The simplest way to take it into account is in changing the line center frequency ω_0 for $\omega_0 + \mathbf{kv}$ ($\mathbf{v}$ is as earlier the velocity of a molecular center of mass and $\mathbf{k} = (\omega/c)\,\mathbf{k}_0$ is the wave vector of the field) and averaging over Maxwellian distribution of the molecular velocities.

A short preamble should be given prior to discussion of other essential element. The line shape of an isolated molecule is $\frac{1}{\pi}\,\mathrm{Re}\int_0^\infty \mathrm{d}t\, \exp(i(\omega - \omega_0)\,t)$; as a result of introducing the Doppler effect the quantity $\mathbf{v}t$ appears and this product accounts for collisional effects occurring during a travel of the center of mass of a molecule along a trajectory has to be written as $\mathbf{R}(t)$. The last quantity is undoubtedly a random value and averaging over the probability of a displacement of the molecular center of mass on the value $\mathbf{R}$ during time t at the initial velocity $\mathbf{v}$ $W(\mathbf{R}, t, \mathbf{v})$, is quite necessary. Then the line shape[45] is

$$g(\Omega) = \frac{1}{\pi}\int_0^\infty \mathrm{d}t \int \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{v}\, W(\mathbf{r}, t, \mathbf{v})\, \mathrm{e}^{i\Omega t - i\mathbf{kR}}\ , \quad \Omega = \omega - \omega_0\ . \tag{20}$$

Equation (20) is interpreted as a relation that takes into account the collisional effects on the Doppler line shape.

A more detailed account of collisions leads to the convolution[44–46]

$$g'(\Omega) = \frac{\beta}{\pi}\int \frac{g(\Omega')\,\mathrm{d}\Omega'}{(\Omega - \Omega')^2 + \beta^2} \tag{21}$$

with the function $g(\Omega)$ from Eq. (20) and β being the Lorentzian line halfwidth. For a line wing β is replaced by the corresponding function $\beta(\Omega)$ (see Ref. 14).

To this end, the line shape calculation has to be preceded by calculation of W. This function is the solution of the Boltzmann equation.[32,47]

$$\frac{\partial W}{\partial t} + \mathbf{v}\ \mathrm{grad}\ W = \mathrm{St}(W) \tag{22}$$

which involves the collision integral $\mathrm{St}(W)$. If one assumes that $\mathrm{St}(W) = 0$ one arrives at the procedure from the beginning of this section (it was referred to during the discussion of Eq. (17)). It is possible to use the equation similar to the Fokker–Planck equation,[32,48] the approximation of "light active molecules in a gas of heavy buffer molecules"[32] and so on. Very popular[45] is the version from Ref. 49; though formally it describes the situation of "heavy active molecules in a light buffer gas", its approximation capabilities are much wider. Of course, careful calculations of the line shape at high altitudes with the properly chosen $\mathrm{St}(W)$ in Eq. (20), adequate to the physical conditions of the problem, is the necessary element of the analysis.

Now we should be convinced that the physical grounds of Eq. (20) (and Eq. (21)) result in a spatial dispersion (4).

The proof starts with the solution of Eq. (6) in the first order of the theory of perturbations over parameter (9)

$$\mathbf{P}(\mathbf{r}, \omega) = \int_0^\infty \mathrm{d}t\ \mathrm{e}^{i\omega t}\ \mathrm{Tr}\ \hat{\rho}^{(0)}\, \frac{1}{i\hbar} \times$$

$$\times \left(\sum_{\alpha} \mathbf{E}(\mathbf{r}_\alpha, \omega)\, e_\alpha \mathbf{r}_\alpha,\ \exp[\,-\,(t/i\hbar)\, \hat{H}_0] \times\right.$$

$$\left.\times \sum_{\alpha'} e_{\alpha'}\mathbf{r}_{\alpha'}\delta(\mathbf{r} - \mathbf{r}_{\alpha'})\ \exp[(t/i\hbar)\, \hat{H}_0]\right]. \tag{23}$$

Further some standard simplifications[14] of Eq. (23) are done.

The long wave approximation for intramolecular degrees of freedom and interpretation of the active molecule as a dynamic subsystem as well as obvious isotropy of the medium enable one to separate out $\mathbf{E}(\mathbf{R}, \omega)$ from Eq. (23) with the former sense of $\mathbf{R}$. The factor "line intensity S" and $\exp(-i\omega_0 t)$ will appear (the latter comes from the interaction representation for $\exp(\pm (t/i\hbar)\, \hat{H}_0)$). Quite remarkable here is the role played by $\delta(\mathbf{r} - \mathbf{r}_{a'})$. It is evident from the above facts that it can be changed for $\delta(\mathbf{r} - \mathbf{R})$. Of course, $\mathbf{R}$ is considered to be the classical quantity and δ–function during the averaging of Eq. (23) over the elementary volume, necessary for the transition to macroscopic electrodynamics, will make one to consider only those trajectories of molecular centers of mass which begin at the point $\mathbf{r}$. In other words, it will be necessary to seek the probability of the displacement on $\mathbf{R} - \mathbf{r}$ (i.e., $W = W(\mathbf{r} - \mathrm{R}, t, \mathbf{v})$). Finally, it has to be noted that the operation $\mathrm{Tr}\hat{\rho}^{(0)}$ includes $\int \mathrm{d}\mathbf{R}\, \mathrm{d}\mathrm{v}\, W(\ \dots\ )$ since $\mathbf{R}$ is a classical quantity.

Introducing all the quantum operations and the integration over $\mathbf{v}$ into the definition of f from Eq. (4), taking into account the dependence of the system field response just on $(\mathbf{r} - \mathrm{R})$, separating $\int \mathrm{d}\mathbf{R}$ from Tr, and performing an obvious substitution of the integration variable we shall see Eq. (4).

The absorption coefficient of an individual line is equal to $Sg(\varkappa)$, and now we have its explicit form (20). Actually, just this gives a possibility of writing $\Gamma(\Omega, \lambda)$ for quantity (10): now by comparing Eqs. (4), (11), (10), and (20) we obtain

$$\Gamma(\varkappa, \lambda) = \frac{Sc}{4\pi^2\omega}\, i \int\limits_0^\infty \mathrm{d}t \int \mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{v}\, \exp(i\Omega t - i\lambda\mathbf{R})\, W(\mathbf{R}, t, \mathbf{v}). \quad (24)$$

Total function $\Gamma(\omega, \lambda)$ is a sum of Eqs. (24) over the absorption lines. Generalization of Eq. (24) into Eq. (21) is quite evident, thus for $\mathrm{Re}\,\Gamma$ one only needs to write a convolution as in Eq. (21) with quantity (24) instead of $g(\Omega')$ while $\mathrm{Im}\,\Gamma$ can be found using the dispersion relations. (It is worthwhile to note here the problem on the ray refraction which could probably be of interest (the calculation of $\mathbf{k}_0$ in Eq. (1)) in the medium with the spatial dispersion).

The physical meaning of Eq. (4) in the case of small pressures is rather clear. Indeed, the spatial dispersion appears when it is impossible, for some reasons, to use the long wave approximation for the centers of mass.[14,41] A large length of free paths and the interaction between the molecule and the resonance field just during the free flight are the circumstances making the long wave approximation to be inapplicable. It was emphasized in Ref. 14 that the spatial dispersion in the line wings and that considered now are the limiting cases (with respect to the value Ω) of the same problem "centers of mass of molecules".

5. EMISSION COEFFICIENT AT SMALL PRESSURE

Let us return to the discussion of Eq. (10). As it turns out[14] Eq. (10) is reduced to Eq. (2) under two conditions, namely, (i) there is no spatial dispersion, i.e., Eq. (4) changes into Eq. (5), (ii) there exists the thermodynamic equilibrium, i.e., density matrix (13) and Eq. (4) for the correlator are valid.

In Ref. 14 there was given a detailed discussion of the spatial dispersion of the imaginary part of the dielectric constant inherent in the band wings, and there are convincing experimental evidences of its existence, and among them the breakdown of the local thermodynamic equilibrium. Similar numerical and experimental analysis of the spatial dispersion typical of low pressures is yet to be done.

There is one quite evident cause of breaking the condition (ii) in the upper layers of the atmosphere, namely, the photochemical reactions (similar question was discussed in Ref. 50). The beams of charged particles, etc. can certainly change the quantum state population. Now we need to keep in mind Eq. (12) and a small modification of its derivation is required. It takes into account the fact that in an ordinary for the gas phase binar approximation the line shape appears as a statistical average of the δ–function the argument of which is the golden Fermi rule in the problem on two colliding molecules.[14] As a result, the main formal element is conserved for understanding the relationship between Λ and κ.

As a result we obtain

$$\Lambda = \frac{1 + \exp(-\hbar\omega/k\Theta)}{1 - \exp(-\hbar\omega/k\Theta)} \sum_{nm} \frac{1 + \exp(-\hbar\omega/k\Theta)\,\sigma_{mn}}{1 + \exp(-\hbar \mathrm{w}/k\Theta)} \times$$

$$\times \frac{1 - \exp(-\hbar\omega/k\Theta)}{1 - \exp(\hbar\omega/k\Theta)\,\sigma_{mn}}\, \mathrm{Im}\, \tilde{\Gamma}_{mn}\ . \quad (25)$$

The numbers n and m are, as earlier, the quantum indices of the active molecule and $\sum\limits_{nm}$ is the sum over lines (n denotes the lower state); $\sigma_{mn} = \sigma_m/\sigma_n$, $\sigma_n = \rho_n/\rho$ is the ratio of the population appeared as a result of the external forces to the equilibrium population (only the intramolecular degrees of freedom are considered here). The quantity Γ_{mn} is constructed like Eq. (24) with the only difference that a line intensity factor σ_n is added.

There is one more, and universal, cause of the systematic deviation from Eq. (13), namely, the thermodynamic when the number of molecules in the unit volume is comparatively small. Of course, the electromagnetic fluctuations discussed in Sec. 2 are "instantaneous" as compared with the thermodynamic ones and therefore they can be directly introduced into Eq. (10).

The fluctuation problem of the distribution function is well known in physical kinetics,[32] and it again brings us back to Eq. (22). The solution that follows is done with two simplifications taken into account. First, $\varkappa$ is believed to be a stable distribution,[51] i.e.,

$$\int W(\mathbf{R}_1, t_1, \mathbf{v})\, W(\mathbf{R}_1 + \mathbf{R}, t_1 + t, \mathbf{v})\, \mathrm{d}\mathbf{R}_1 \mathrm{d}t_1 = \tau W(\mathbf{R}_1, t_1, \mathbf{v})\ ,$$

where τ is the relaxation time. Second, taking the standard interpretation of relaxation of systems in states which are close to an equilibrium one assumes that in the equation similar to Eq. (22) for the thermodynamic–fluctuations correlator $\mathrm{St}(W) = (-1/\tau)W$.

Other approximations are, in fact, only technical ones and in the final expression the quantity

$$N \frac{|D|^4}{\hbar^2} \rho_n^{(0)} [\mu_m - \mu_n \exp(-\hbar\omega/k\mathrm{H})] \tag{26}$$

with summation over lines should be added to the term $c\,\mathrm{th}\,(\hbar\omega/k\Theta)(\mathrm{Im}\,\Gamma)^2$ in the numerator of the integrand in Eq. (10) corresponding to Eq. (14). As earlier N is the number of active molecules per unit volume, D_{nm} are the matrix elements of the dipole moment and ρ is the same as in Eq. (15). Then

$$\mu_n = \frac{\tau_n}{\upsilon_0^2 \lambda} \frac{1}{2\pi^3} \int k \mathrm{d}k \int \mathrm{d}\Omega' g(\Omega', k)\, B(\Omega - \Omega', k, \lambda)$$

with line shape (20) (or (21), if necessary), and the relaxation time is labelled by the index of the state, υ_0^2 is the rms velocity and

$$B(\Omega - \Omega', k, \lambda) = \int_0^\infty \mathrm{d}z\, \mathrm{e}^{-\tau/z} \frac{\sin(\lambda\upsilon_0 z) \sin(k\upsilon_0 z) \cos((\Omega - \Omega')z)}{z^2}.$$

6. CONCLUDING REMARKS

The conditions existing in the upper atmosphere introduce rather nontrivial features into the description of the emission and absorption of light. Below we only name the problems arising here.

The problems on the line shape, and on the spatial dispersion and its effect on the absorption and emission coefficients (Eqs. (20), (21), (24), (10), and (11)) have to be preceded by a careful choice of the statistical model for the collisional integral in Eq. (22).

Only detailed numerical analysis of the problem for different spectral regions, absorbing gases and models of the atmosphere will enable one to establish how essential is the spatial dispersion and the fluctuations of distribution (Eqs. (10) and (26)) for the absorption coefficient and for the case of broken local thermodynamic equilibrium.

The change of the emission coefficient caused by the photochemical reactions and by other external factors (Eq. (25)) can be very attractive for solving corresponding inverse problems (for example, for limb measurements from satellites).

There appear rather long paths in many applied problems of atmospheric optics and the necessity could arise of taking into account the refraction along the paths. Its value for the medium with the spatial dispersion (similar to that in Eq. (24)) has not been yet evaluated.

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