

# Infrared radiation transport in a nonequilibrium molecular gas

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(Submitted 20 July 1977)

Zh. Eksp. Teor. Fiz. 74, 1257-1263 (April 1978)

The transport of infrared radiation in a molecular gas when the local thermodynamic equilibrium is disturbed is investigated. It is shown that under certain conditions this problem reduces to the two-level problem solved in the theory of resonant-radiation transport. Within the terms of the distribution function over the optical thickness, general expressions are obtained for the probability of "shooting through" a quantum from a gas layer and for the concentration of the vibrational excited molecules. In the case of a Lorentz or Doppler contour of the spectral line, the concentration of the vibrationally excited molecules in a plane layer of gas and of the radiation fluxes produced by them is obtained.

PACS numbers: 51.10.+y

The infrared molecular spectrum consists of a large number of lines, each of which corresponds to a definite vibrational-rotational transition. The absorption coefficient of a molecular gas is therefore a rapidly oscillating function of the frequency. The theory of the transport of infrared radiation in a gas medium under conditions of thermodynamic equilibrium has been sufficiently well developed.<sup>[1,2]</sup> In the present paper, using a procedure based on the distribution function over the optical thickness,<sup>[3,4]</sup> this theory is extended to include the case of a molecular gas that is not in thermodynamic equilibrium. Allowance for the disequilibrium of the gas medium is based on the results of the theory of transport of resonant radiation.

1. By virtue of the large difference between the rates of the vibrational and rotational relaxation<sup>[10]</sup> there exists a large range of gas densities in which the frequency of the rotational relaxation is much higher, and the frequency of the vibrational relaxation is much lower, than the frequency of the spontaneous emission of the vibrationally excited molecules. In this range, the thermodynamic equilibrium relative to the vibrational levels of the molecules is disturbed, but a uniform distribution over the rotational levels does exist within each vibrational state. We consider the simplest physical situation, when the energy  $\hbar\omega_0$  of the vibrational quantum exceeds considerably the gas temperature  $T$ , and the radiation transport does not influence the number of molecules in the ground state. We shall assume that the radiation of the molecular gas is produced primarily by transitions between the ground and the first excited vibrational levels of the molecules. In this case, the physical picture of the transport of the infrared radiation is identical with that of transport of resonant radiation. The contour of the "emission line" duplicates in this case the structure of the molecular band, i.e., it is the product of a smooth function and a rapidly oscillating function of the frequency.

The concentration of the vibrationally excited molecules is determined by the Biberman-Holstein equation<sup>[5,6]</sup>:

$$\int G(\mathbf{r}, \mathbf{r}') y(\mathbf{r}') d\mathbf{r}' + \beta - (1 + \beta) y(\mathbf{r}) = 0. \quad (1)$$

Here  $\beta = w\tau$  is a parameter, with  $w$  the frequency of the

quenching of the vibrational excitation of the molecules by the collisions, and  $\tau$  the time of spontaneous emission of the vibrationally excited molecule. The Green's function is given by

$$G(\mathbf{r}, \mathbf{r}') = \int_{-\infty}^{+\infty} d(\omega - \omega_0) \int_0^{\infty} k^2 f(k) \exp\left\{-\int k dl\right\} dk \times \left[4\pi|\mathbf{r} - \mathbf{r}'|^2 \int_{-\infty}^{+\infty} d(\omega - \omega_0) \int_0^{\infty} k f(k) dk\right]^{-1}. \quad (2)$$

This form of the expression is based on the results of<sup>[3,4]</sup>, where a theory of infrared radiation transport is developed on the basis of the distribution function over the optical thickness of the gas layer. In (2),  $f(k)dk$  is the probability that the absorption coefficient of the gas at a given frequency has a value in the interval from  $k$  to  $k + dk$ ;  $f(k)$  is the distribution function over the optical thickness;  $\omega_0$  is the frequency corresponding to the center of the molecular band; the integral  $\int k dl$  is taken along the line joining the points  $\mathbf{r}$  and  $\mathbf{r}'$ . In the case of a homogeneous gas layer the approximate solution of (1) is of the form<sup>[5,7,8]</sup>

$$y(\mathbf{r}) = \beta / [\beta + D(\mathbf{r})]. \quad (3)$$

The quantity

$$D(\mathbf{r}) = \int \frac{d\Omega}{4\pi} \int_{-\infty}^{+\infty} d(\omega - \omega_0) \int_0^{\infty} k f(k) \exp\left\{-\int k dl_\Omega\right\} dk \times \left[\int_{-\infty}^{+\infty} d(\omega' - \omega_0) \int_0^{\infty} k' f(k') dk'\right]^{-1} \quad (4)$$

is the probability of "shooting through" a quantum, i.e., the probability, averaged over the angles, that a photon radiated into the point  $\mathbf{r}$  will leave the gas layer without being absorbed, the integral  $\int k dl_\Omega$  is taken from the point  $\mathbf{r}$  to the boundary of the gas layer, and the vector joining the point  $\mathbf{r}$  with the point on the boundary lies in the solid-angle element  $d\Omega$ . The criterion for the applicability of formula (3) is, generally speaking, not quite clear. If the probability that the photon will pass through the entire gas layer without being absorbed<sup>[1]</sup> is  $D_0 \ll \beta$ , then this formula is already wrong near the gas-layer boundary, where  $D(\mathbf{r}) \approx 1/2$ . In the case of "pure scattering" ( $D_0 \gg \beta$ ) formula (3) seems to work well at all points of the gas layer. The question of its validity

is considered in sufficient detail in [11,12].

Let us find the function  $y(x)$  for a planar layer of gas of linear molecules with constant parameters (temperature, density), and with individual spectral lines of Lorentz shape at large optical layer thicknesses at the line centers. The width of the spectral line will be assumed small compared with the distance between neighboring lines. We use two approaches, the regular Elsasser [13] model and the random Goody model, [14] both modified with account taken of the frequency dependence of the intensity of the spectral lines. [3, 4, 15] Within the framework of the regular model, the probability of the absorption coefficient of the gas layer being in the interval from  $k$  to  $k+dk$  is equal to the probability of landing in the corresponding frequency interval.

For a Lorentz contour of the spectral line, the distribution function  $f(k)$  is defined by the expression [16]

$$f(k) = \frac{\eta \hbar \gamma}{4Bk[(kL - \eta)(\eta(\pi \hbar \gamma / 4B)^2 - kL)]^{1/2}}, \quad (5)$$

in which  $L$  is the thickness of the gas layer,  $\eta$  is its optical thickness at frequencies corresponding to the minima of the spectral lines,  $\gamma$  is the line width, and  $B$  is the rotational constant of the molecule. The dependence of the parameter  $\eta$  on the frequency is determined by the population of the rotational levels and was obtained in [15]. The random model presupposes a chaotic arrangement of the spectral lines. Within the framework of this model the distribution function  $f(k)$  turns out to be [3, 4]

$$j(k) = \frac{L}{\pi} \int_0^{\infty} \exp\left\{-\left(\frac{2\eta t}{\pi}\right)^2\right\} \cos\left(kLt - \left(\frac{2\eta t}{\pi}\right)^2\right) dt. \quad (6)$$

The random model is an approximate calculation method. This method is convenient when several molecular bands overlap, and also when the spectral line has a non-Lorentzian contour and the use of the regular model is therefore difficult. The error of this method can be estimated by comparing the results of the random and regular models in the situation considered here (transitions between two vibrational levels of the linear mode, Lorentz contour of the spectral line), when the regular model is practically exact.

The plot of  $y(x)$  at different values of the two parameters of the problem, namely the maximum value  $\eta_m$  of

$\eta$  and

$$\kappa = \frac{\pi \hbar \gamma}{4\beta B (\pi \eta_m)^2 (2e)^2}$$

obtained with the aid of (3) is shown in Fig. 1. The quantity  $1/\kappa^2$  is the product of the maximum value of the optical thickness of the gas layer and the parameter  $\beta$ . If  $\eta_m \rightarrow 0$ , then the random and regular models produce the same result. The reason is that at  $\eta_m \ll 1$ , i.e., at a small optical gas-layer thickness, the radiation process in the frequency region between the spectral lines is concentrated in individual lines. Therefore the use of any particular model of the molecular band does not affect the obtain value of the concentration of the vibrationally excited molecules. In this case formula (3) yields for the function  $y(x)$  the analytic expression

$$y(x) = \frac{[x(L-x)]^{\eta}}{[x(L-x)]^{\eta} + \kappa L^{\eta} 2^{\eta+1} \Gamma(\eta/2) [x^{\eta} + (L-x)^{\eta}]}. \quad (7)$$

3. Let us determine the radiation fluxes, integrated over the frequencies, produced by a plane layer of a gas of linear molecules under the considered conditions. The intensity of the radiation emerging from the gas layer at a right angle to its boundary is given by

$$I = 2j_{\omega_0}(T) \int_{-\infty}^{+\infty} d(\omega - \omega_0) \int_0^{\infty} f(k) k dk \int_0^L y(x) e^{-kx} dx, \quad (8)$$

where

$$j_{\omega}(T) = \frac{\hbar \omega^3}{4\pi^2 c^2} (e^{\hbar \omega / T} - 1)^{-1}$$

is the radiation flux from an absolutely black body with temperature  $T$ . Formula (8) differs from the thermodynamic-equilibrium formula in that the integrand contains the function  $y(x)$ .

We introduce the concept of the equivalent width  $W$  of the molecular band, such that the following equality holds:

$$I = 2j_{\omega_0}(T) W.$$

The band width defined in this manner takes into account automatically the disturbance of the thermodynamic equilibrium in the gas. Its value as functions of the parameters  $\eta_m$  and  $\kappa$  are shown in Fig. 2a. Figure 2b

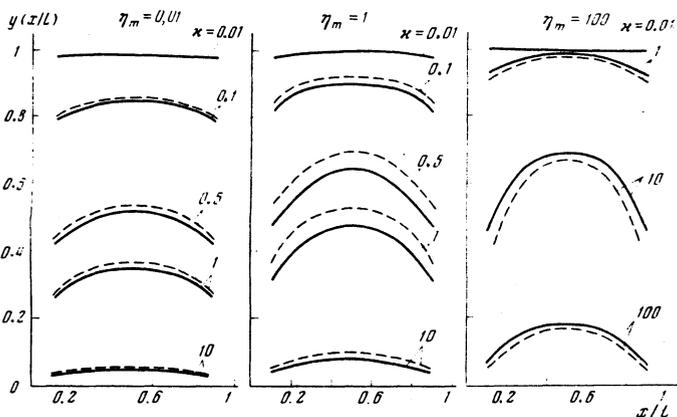


FIG. 1. Distribution of the concentration of the vibrationally excited molecules in a plane layer of a molecular gas.

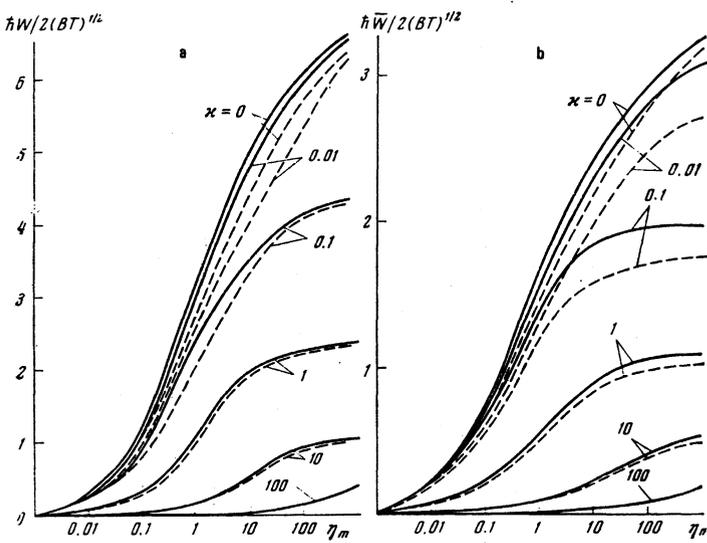


FIG. 2. Equivalent width of individual vibrational-rotational band of linear molecules in the absence of thermodynamic equilibrium: solid curve—regular model, dashed—random model.  $W$ —equivalent band width,  $\bar{W}$ —equivalent band width averaged over the angles of photon emission from the gas layer.

shows the band width  $\bar{W}$  averaged over the angles of emission of the photon from the gas layer.

The maximum difference between the results of the regular and random models takes place when the equivalent band width coincides with its equilibrium value.<sup>2)</sup> In particular, at  $\eta_m \ll 1$  and  $\kappa \ll 1$  and at  $\eta_m \gg 1$  and  $\kappa \eta_m^{1/2} \ll 1$ . In this case the vibrationally excited molecule concentration is at equilibrium in the internal region of the gas layer, where the flux of the outgoing radiation is formed in the main. Therefore the radiation flux produced by the gas also coincides with its equilibrium value, although the density of the vibrationally excited molecules decreases sharply on the layer boundary.

With decreasing parameter  $\beta$ , i.e., with increasing degree of disequilibrium of the molecular gas, the difference between the results of the regular and random models decreases. In the limiting case when the vibrationally excited molecules disintegrate in practice only on account of the photon emission, and the radiation is produced by the entire volume of the gas (particularly at  $\eta_m \ll 1$ ,  $\kappa \gg 1$  and  $\eta_m \gg 1$ ,  $\kappa \gg (\eta_m \ln \eta_m)^{1/2}$ ), the regular and random models yield the same line width:

$$\frac{\hbar W}{2(BT)^{1/2}} = 2 \left( \frac{2e}{\pi^2} \right)^{1/2} \frac{\eta_m^{1/2}}{\kappa}, \quad \bar{W} = \frac{W}{2}. \quad (9)$$

The results obtained for the equivalent band width are valid if the radiation fluxes are produced mainly by the gas-layer region in which the concentration of the vibrationally excited molecules is determined by formula (3). Therefore in the case of a semi-infinite medium, when this formula is not valid near the layer boundary, it is necessary to compare the radiation fluxes produced by the internal and boundary regions. This comparison shows, incidentally, that under the considered physical conditions (large optical thickness of the gas layer at the centers of the spectral lines and a distance between the neighboring lines much larger than their width) the results are valid at all values of the parameters  $\eta_m$  and  $\kappa$ .

The results for the equivalent width of the molecular band were obtained under the assumption that the function  $j_\omega(T)$  is constant within the limits of the band. This is true if the equilibrium value of the equivalent band width is much less than the gas temperature. We have neglected also the radiation due to transitions between higher vibrational levels. At large values of the parameter  $\eta_m$  and at a strong difference between the zero-point frequencies of the various transitions this limits the considered temperature band from above by the condition  $\eta_m e^{-\hbar\omega_0/T} \ll 1$ . The limitation is less stringent ( $e^{-\hbar\omega_0/T} \ll 1$ ) at  $\eta_m \lesssim 1$ .

5. The developed theory enables us to find the concentration of the vibrationally excited molecules and the radiation fluxes of the gas layer also in the case of a Doppler contour of the spectral line, provided that the individual lines in the band do not overlap.<sup>3)</sup> The distribution function  $f(k)$  corresponding to this case takes, in the region of values of  $k$  that make the main contribution to the quantum emission probability  $D(\nu)$ , the form

$$f(k) = \frac{\hbar\gamma_D}{2Bk(\ln 2)^{1/2}} \left( \ln \frac{u_D}{kL} \right)^{-1/2} \quad (10)$$

and is independent of the relative locations of the lines. In (10),  $\gamma_D$  is the Doppler line half-width, and  $u_D$  is the optical thickness of the gas layer in the centers of the spectral lines. Its frequency dependence in the considered case of a plane layer of a gas of linear molecules with constant parameters is determined by the formulas of [15].

Calculating the probability of the "shoot-through" quantum emission with the aid of formula (4) and using next formula (3), we obtain the following expressions for the density of the vibrationally excited molecules and the equivalent width of the molecular band:

$$y(x) = \frac{4\alpha x(L-x)}{L^2 + 4\alpha x(L-x)} \quad (11)$$

$$W = \frac{SL\beta}{[\alpha(1+\alpha)]^{1/2}} \ln \left( \frac{(1+\alpha)^{1/2} + \alpha^{1/2}}{(1+\alpha)^{1/2} - \alpha^{1/2}} \right) \quad (12)$$

Here  $\alpha = 2u_{D_{\max}}\beta/\pi^{1/2}$ ,  $u_{D_{\max}}$  is the maximum value of the

parameter  $u_D$ , and  $S$  is the band intensity. The band width  $\bar{W}$  averaged over the angles of photon emergence from the gas layer is equal to  $W/2$ .

Formula (12) is valid only at  $\beta \ll 1$  and does not contain the case of thermodynamic equilibrium as the limit.<sup>4)</sup> At  $\beta \gg 1$  the radiation flux is formed mainly near the boundary of the gas layer, where the concentration of the vibrationally excited molecules is no longer determined by (11).

The physical situation considered in the present paper is realized at gas densities  $N \sim 10^{12}$  to  $10^{17}$  cm<sup>-3</sup> and at temperatures  $T \sim 150$  to  $300$  K, ranges which are characteristic of the upper atmospheres of planets. The results obtained here can be generalized to include the case of an inhomogeneous molecular gas and used in the investigation of upper atmospheres.

The authors thank V. I. Kogan and B. M. Smirnov for valuable discussions.

<sup>1)</sup>This case is referred to as "semi-infinite medium" in the theory of resonant-radiation transport. On the contrary, the case  $D_0 \gg \beta$  is called "pure scattering."

<sup>2)</sup>The equilibrium values of the band width  $W$  are given in the papers of Smirnov and Shlyapnikov.<sup>[3,4,15]</sup>

<sup>3)</sup>This case was considered earlier by Shved,<sup>[17]</sup> where a system of equations was analyzed for the populations of the vibrational-rotational levels of the molecules.

<sup>4)</sup>In the case of thermodynamic equilibrium, the known formulas for the radiation flux of an equilibrium gas<sup>[10]</sup> make it

possible to obtain the following relations for the equivalent band widths:

$$W = \frac{\pi^h}{2} SL \frac{\ln u_{D \max}}{u_{D \max}} \quad \bar{W} = \frac{W}{2}$$

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Translated by J. G. Adashko

## Effect of electric field on the fluorescence of impurity anthracene crystals

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(Submitted 1 September 1977)

*Zh. Eksp. Teor. Fiz.* **74**, 1264-1271 (April 1978)

The effect of an electric field on the fluorescence spectra of the impurity and of the matrix is investigated for anthracene single crystals with tetracene and pentacene as impurities, under conditions of unipolar injection and on the boundary of the blocking electrode. The introduction of impurities into an anthracene crystal produces additional lattice defects on which excitons and carriers are localized. An external electric field, by changing the conditions at the interface between the molecular crystal and the electrode, as well as the number of carriers localized on the defects in the interior of the crystal, modulates the intensities of the impurity and host fluorescence. The localization of the charge on a lattice defect alters the rate of the energy-transfer constant of the singlet excitations from the matrix molecules to the impurity molecules, or to a mixing of the neutral excited states with states charge transfer. It is shown that by investigating the effect of the electric field on the fluorescence of the impurity anthracene crystals it is possible to investigate not only the processes whereby excitons interact with the carriers, but also the lattice-structure defects that are not revealed in ordinary fluorescence spectra.

PACS numbers: 78.50.Ec, 78.60.Fi

Introduction into anthracene crystal of impurities that intercept singlet electrons leads to quenching and modification of the structure of the fluorescence spectrum of the host and to the appearance of impurity

fluorescence. The fluorescence spectrum of the base differs from that of the spectrum of the pure crystal more the larger the perturbing action of the impurity molecule on the action and the larger the impurity