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STANDARD PROBLEM OF RADIATIVE TRANSFER IN A VIBRATION-ROTATION BAND IN A PLANETARY ATMOSPHERE UNDER NON-LTE CONDITIONS

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ABSTRACT

We attempt here to lay foundations of general theory of radiative transfer in a vibration-rotation band in a planetary atmosphere by formulating and solving corresponding standard problem that is an integral equation for the source function. We introduce a convenient dimensionless vertical coordinate and four similarity parameters to describe the dependence of the source function on height. We propose formulas approximating the calculations of the source function.

1. INTRODUCTION

For molecules emitting from their vibrational states the decrease of molecular collision frequency with height results in a nonequilibrium (non-Boltzmannian) population of these states in the middle planetary atmosphere, that is named as a breakdown of the local thermodynamic equilibrium (LTE). In order to determine the vibrational state populations a set of kinetic equations should be solved. If the optical thickness of the non-LTE (NLTE) layer is large, simultaneous solution of kinetic equations and radiative transfer equation is necessary. There are many calculations of the NLTE vibrational populations for particular vibration-rotation (v.-r.) bands in planetary atmospheres. However, there is no general theory of radiative transfer in a v.-r. band under the NLTE conditions. In distinction from the theory of radiative transfer in atomic line, developed for homogeneous media (e.g., Ivanov, 1973), the general feautures of the source function in inhomogeneous planetary atmosphere for radiative transfer in a v.-r. band have not been investigated at all. We attempt here to make such investigation by formulating and solving a standard problem that is an integral equation for the source function. The source function was studied as a dependence on a convenient dimensionless vertical coordinate and four similarity parameters. The variety of these parameters was taken wide to cover all possible values that can be realized in planetary atmospheres including hypothetical atmospheres of extrasolar giant planets. We state here a standard problem which deals only with the main features both of radiative transfer in a band and atmospheric structure, neglecting details both of individual band structure and of real profiles of atmospheric composition and temperature. The standard problem is formulated for an isothermal atmosphere without an external source of excitation of vibrational states. Thus the NLTE effect occurs due to the "open" upper boundary of the atmosphere and results in decrease of vibrational population comparing to the LTE conditions.

2. FORMULATION OF STANDARD PROBLEM

We consider a semi-infinite plane-parallel isothermal atmosphere with the exponentially decreasing frequency of molecular collisions. We use the two-level model of vibrational states of the parallel band of a linear molecule (without the Q-branch). Radiative transitions between these two levels form v.-r. band (Fig. 1). We suppose that rotational lines do not overlap and use the assumption of rotational LTE.

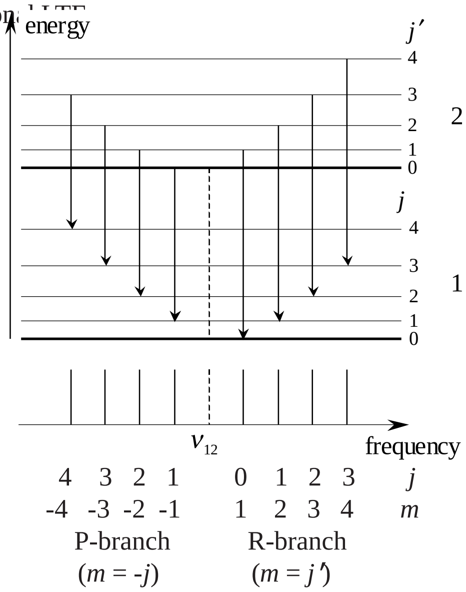

Fig. 1. Scheme of rotational structure of lower and upper vibrational states, v.-r. transitions and spectrum of v.-r. band, considered in our study.

We introduce the dimensionless source function

$$S = \frac{g_1 n_2}{g_2 n_1}, \tag{1}$$

where n_2 and n_1 are the populations of the upper and lower vibrational states, respectively, g_2 and g_1 are the statistical weight factors of these states. The population of the upper vibrational state is controlled by a balance of excitation and de-excitation processes, among which we consider only absorption and emission of photons and inelastic thermal collisions of molecules. When the collisions are very frequent the LTE approximation is valid. Vibrational populations are therefore consistent with the Boltzmann law

$$\frac{\bar{n}_2}{\bar{n}_1} = \frac{g_2}{g_1} \exp\left(-\frac{h\nu_{12}}{kT} \right), \tag{2}$$

and, consequently,

$$\bar{S} = \exp\left(-\frac{h\nu_{12}}{kT} \right), \tag{3}$$

where overbar denotes an equilibrium value. Here h is the Planck constant, k is the Boltzmann constant, ν_{12} is the frequency of the vibrational transition 1→ 2, and T is the local kinetic temperature of the atmosphere.

Eleven input parameters are involved in the standard problem: 5 of them correspond to molecular characteristics – ν_{12}, g_2/g_1, M (mass of emitting molecule), A_{21} (Einstein coefficient of spontaneous emission for the transition 2→1), B (rotational constant); 4 describe planetary atmosphere – T, g (gravity), $\bar{M}$ (mean molecular mass of the atmosphere), c_V (mixing ratio of emitting molecule); 2 describe molecular collisions – k_{21} (rate constant for the transition 2→1) and $\Delta\nu_{L,s}$ (Lorentz line halfwidth for standard spectroscopic conditions: T = 296 K and pressure p = 1 atm). It can be shown that the source function depends only on the 4 dimensionless similarity parameters b, d, τ_N and a_N , composed of these 11 input parameters.

The parameter of band structure,

$$b = \frac{1}{2}\sqrt{\frac{hB}{kT}}\,, \tag{4}$$

describes the distribution of line intensities in a band. The parameter of equilibrium population of vibrational states, that appears in Eq. (2), is

$$d = \frac{h\nu_{12}}{kT}\,. \tag{5}$$

The main parameter characterizing deviations from LTE is

$$\tau_N = \frac{c^2 h}{4\pi^{3/2}\sqrt{2e}} \frac{g_2}{g_1} \frac{c_V A_{21}^2 b e^{b^2}}{\nu_{12}\Delta\nu_D \bar{M}\, g\, k_{21} d}\,. \tag{6}$$

The value τ_N is approximately equal to the optical depth for the most intensive line of a band at a height where the radiative lifetime of vibrational state of a molecule equals the collisional one. We introduce dimensionless pressure and height,

$$y = p/p_N \text{ and } \zeta = -\ln y\,, \tag{7}$$

where p_N is the pressure corresponding to τ_N. The forth parameter a_N is the Voigt parameter at pressure p_N:

$$a_N = \frac{\Delta\nu_{L,s} A_{21}}{\Delta\nu_D k_{21} n_s}\,, \tag{8}$$

where n_s is the molecular concentration for standard spectroscopic conditions. The parameter a_N describes the effect of collisional broadening of line relatively to Doppler broadening.

The ranges of the variety of the similarity parameters are determined by the ranges of the input parameters, and are: d ~ 3–150, b ~ 0.005–0.5, τ_N ~ 0–10^{15}, a_N ~ 10^{-12}–10^4.

The integral equation for the source function is

$$S(y) = \frac{\lambda(y)}{2}\int_0^\infty dy' K(y,y')S(y') + \left(1-\lambda(y)\right)\cdot \bar{S}\,, \tag{9}$$

where

$$\lambda = \frac{1}{1+y}\,, \tag{10}$$

$$K(y,y') = \int_{-\infty}^{\infty} dx\, U(a_N y, x) \sum_{m=-\infty}^{\infty} u_m \left| \frac{\partial E_2\left[\theta_m(y,y')\right]}{\partial y'} \right|, \tag{11}$$

$$E_2(t) = \int_0^1 d\mu\, e^{-t/\mu}\,, \tag{12}$$

$$\theta_m(y,y') = \tau_N \mathsf{v}_m \left| \int_{y'}^{y} dy'' U(a_N y'', x) \right|, \tag{13}$$

$$u_m = \frac{|m|}{Q(b)} \exp\left(-b^2\left((2m+1)^2-1\right)\right), \tag{14}$$

$$\mathsf{v}_m = \sqrt{\frac{\pi e}{2}}\frac{|m|}{bQ(b)} \exp\left(-b^2(2m-1)^2\right) \Big/ \left(1+\frac{8b^2 m}{d}\right)^2, \tag{15}$$

U(a, x) is the normalized Voigt function and *Q(b)* is the rotational partition function.

3. FEATURES OF THE SOURCE FUNCTION

The dependence of $S(y)$ on the similarity parameters b, d, τ_N and a_N was studied using numerical solution of Eq. (9).

The ratio $S/\bar{S}$ varies with d not more than 10%. Therefore, the d-dependence of S is like that of $\bar{S}$: $S \propto e^{-d}$.

The dependences of $S/\bar{S}$ on a_N and τ_N are illustrated in Fig. 2 and 3, respectively. For the large values of τ_N the lower boundary of the NLTE layer moves up and also the value of S at y = 0 decreases as τ_N increases. In the limit of “optical thin band”, realizig for small τ_N, $S = \bar{S}/2$ at the upper boundary of the atmosphere.

The influence of the band structure on $S(y)$, described by the parameter b, is realized via the coefficients u_m and v_m and also indirectly via τ_N ($\tau_N \propto b$). For the large

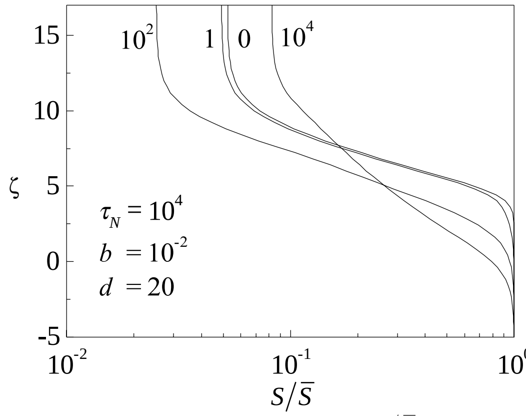

Fig. 2. An example of the dependenses of $S/\bar S$ on a_N. Curves are labeled by a_N.

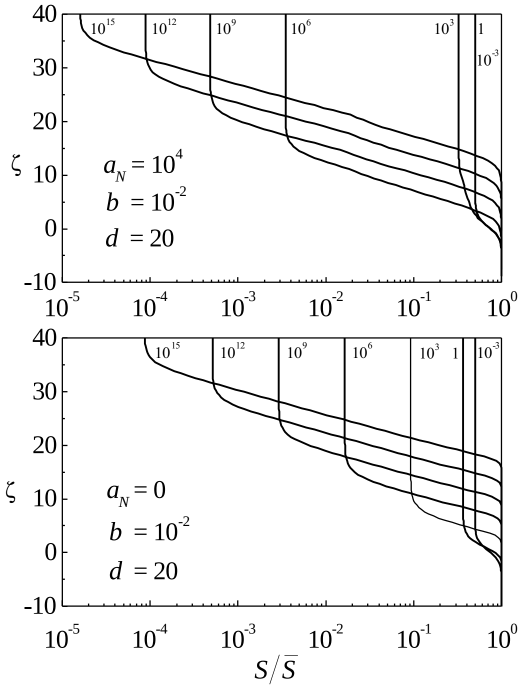

Fig. 3. An example of the dependenses of $S/\bar S$ on τ_N for $a_N = 0$ and $a_N = 10^4$. Curves are labeled by τ_N.

values of b (b > 0.1) the coefficients u_m and v_m decrease rapidly as $|m|$ increases due to the exponents in Eqs. (14) and (15). As a result, not more than several lines of a band are involved in the radiative transfer. That leads to the increase of mean intensity of line in a band and is taken into account in the parameter τ_N (so that $\tau_N \propto b$). For any fixed τ_N $S(y)$ appears to be weakly dependent of b for small b (b < 0.1). However for b > 0.1 the increase of b leads to a strong increase of $S(0)$ and also to the reduction of the height of the lower boundary of the NLTE layer. Therefore, say that an anomalous increase of atmospheric transparency is revealed in a band for b > 0.1. As we have mentioned above, for b > 0.1 not more than several lines with small $|m|$ contribute significantly to the forming of population (Fig. 4), and the contributions of P- and R-branches of a band are different. For b > 0.1 Boltzmannian

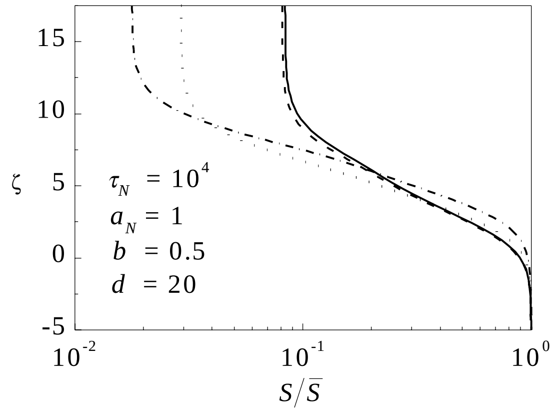

Fig. 4. Illustration of the contribution of different lines of v.-r. band in the forming of population of excited vibrational state in the case of large values of b. Function S (solid curve) is compared with three curves of the source function that have been obtained by approximating the band by two lines only: lines of P-branch with m = -1 and -2 (dashed curve) ; lines of R-branch with m = 1 and 2 (dash-dotted curve); lines of P- and R- branches with m = -1 and 1, respectively (dotted curve).

population of rotational levels decreases rapidly as $|m|$ increase because of a large energy distance between the levels. Hence two consequences are (see Fig. 1). 1) The probability of photon absorption in R-branch is greater than in P-branch. 2) The photon emission in P-branch is much more likely than in R-branch. The anomalous increase of atmospheric transparency for b > 0.1 is formed due to the decrease of photon absorption in P-branch, coupled with the increase of photon emission in it.

4. APPROXIMATE FORMULAS

For small values τ_N the source function appears to be independent of all similarity parameters. In this case, the source function may be approximated by the function

$$S^*(y) = \bar S \,\frac{y+1/2}{y+1}. \qquad (16)$$

The smaller is τ_N the smaller is relative error of this approximation: starting from 40% for $\tau_N = 1$ the error reduces down to 8% for $\tau_N = 10^{-1}$ and 1% for $\tau_N = 10^{-2}$.

The dependence of the value of S at $y = 0$ on τ_N and a_N for b < 0.1 may be approximated by the formula

$$2\,\frac{S(0)}{\bar S} = \frac{1}{1+\sqrt[4]{\tau_N}\,(1+0.6\sqrt[4]{a_N})} + \frac{1}{1+10\,\tau_N/a_N}. \qquad (17)$$

It is enough to use only the first term in r.h.s. of Eq. (17) to estimate $S(0)$ with accuracy better than 30% for $a_N < 10^2$. Moreover the accuracy of estimation increases as a_N decreases and τ_N increases. The second term in r.h.s. of Eq. (17) is needed for estimating $S(0)$ for $a_N > 10^2$ that are scarce in planetary atmospheres.

For solving radiative transfer problems in planetary atmospheres it is important to know the height, below which the LTE approximation is valid. For this purpose we have derived a formula for estimating at $b < 0.1$ the height y below which S may be approximated by the value $\bar{S}$ with specified relative accuracy δS in the $10^{-6} - 10^{-1}$ range. The formula is

$$y = A\left[\frac{1}{1+C\sqrt{\tau_N}} + \frac{1}{1+\sqrt{\tau_N / a_N}}\right], \qquad (18)$$

$$A = 1/(2\delta S) - 1,\ \ C = 2A\sqrt{\delta S}\,,\ \ \delta S = \left(\bar{S} - S(y)\right)/\bar{S}\,.$$

For solving the radiative transfer problems it is also useful to know whether the Voigt profile may be used instead of the Doppler profile. For $a_N < 1$, which are realized most frequently in planetary atmospheres, the error from using Doppler profile is less than 10% for $b < 0.1$ and any τ_N. For $a_N < 0.1$ that is less than 1%.

5. EFFECT OF WEAK ADDITIONAL RADIATIVE TRANSITIONS

For the fundamental bands of polyatomic molecules, transitions from the excited vibrational state down to some underlying vibrational states that belong to the other vibrational mode of the same molecule are possible. An example of these transitions is the “laser” transitions $(00^01) \rightarrow (10^00, 02^00)$ in the CO_2 molecule. The upper state of the transition is identical with that of transition forming the 4.3 μm CO_2 fundamental band. Although the Einstein coefficients of the additional transitions are usually much less than for the corresponding fundamental transition, the influence of these transitions on the source function for the fundamental band appears to be significant for large τ_N. We have estimated approximately the influence of weak additional transitions on the height of the lower boundary of the NLTE layer, modifying correspondingly the formulation of the standard problem. The third vibrational state with the energy which is smaller than that of the upper state 2 in the two-level model has been added. We assume the LTE population of the third state. In the new three-level model the radiative transitions $2 \rightarrow 3$ and $3 \leftarrow 2$ have been entered into the equation for the source function as the additional transitions.

To describe the influence of the additional transitions as a perturbation to the source function we have introduced a small parameter

$$\eta = A_{23} / A_{21}\,, \qquad (18)$$

where A_{23} is the Einstein coefficient of spontaneous emission of the transition $2 \rightarrow 3$. The results obtained by solving the modified equation for the source function are the following. The increase of the parameter η, beginning from its some values, leads to a significant decrease of the height

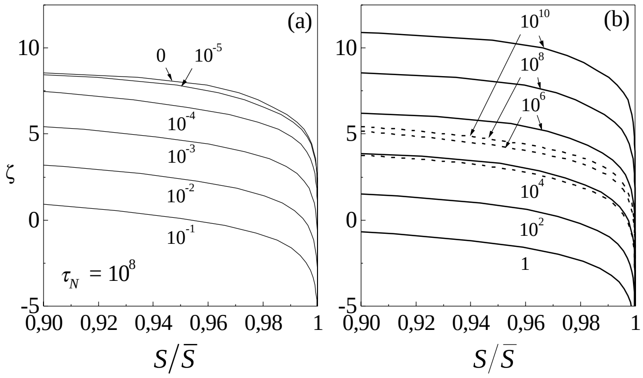

Fig. 5. Influence of weak additional radiative transitions on forming the population of excited vibrational state for $b = 0.03$, $d = 20$, $a_N = 0.3$. The dependences of the $S/\bar{S}$ ratio on the parameters η and τ_N are presented in the figures (a) and (b), respectively. Solid and dashed lines on the figure (b) correspond to $\eta = 0$ and 10^{-3}, respectively.

of the lower boundary of the NLTE layer (Fig. 5a). For a given value of η the increase of this height with τ_N slows down at large τ_N (comparing to the case $\eta = 0$) up to stopping at some values of τ_N (Fig. 5b).

The function $S(y)$ is represented in Fig. 5 for the values of b, d and a_N which are typical for 4.3 μm CO_2 band in the atmospheres of Earth, Venus and Mars. For this band $\tau_N \sim 2{\cdot}10^7$ and $\tau_N \sim 5{\cdot}10^7$ in the atmospheres of Venus and Mars, respectively, but in the terrestrial atmosphere $\tau_N \sim 4{\cdot}10^4$ due to a small value of CO_2 mixing ratio. So far as $\eta \sim 10^{-3}$ for laser transitions, from Fig. 5 it can be seen that the effect of laser transitions leads to decrease the height of the lower boundary of the NLTE layer for the $CO_2(00^01)$ population on Venus and Mars, but has no influence on that in the terrestrial atmosphere. This result is in agreement with the results obtained from realistic models of CO_2 kinetics: the contribution of laser transitions to the forming of the $CO_2(00^01)$ population is negligibly small on Earth (Shved et al., 1998), but is significant on Venus and Mars (Ogibalov and Kutepov, 1989).

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