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VIBRATIONAL NONEQUILIBRIUM RADIATION IN DIATOMIC GASES—I

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Abstract—In the first part macroscopic equations are obtained for the radiation field and internal state of a vibrationally nonequilibrium diatomic gas with the help of a set of kinetic equations for spectral radiation intensity and the one-particle distribution function of molecules. Besides, the basic integral-differential equation is derived for the vibrational energy distribution, which, together with momentum, mass and energy conservation equations, form a closed system.

NOMENCLATURE

$\mathbf{n}$,	unit vector, coinciding in direction with photon momentum;
$J(\mathbf{k})$,	spectral intensity of radiation;
$\omega(\mathbf{k})$,	$= ck$, photon energy;
$E_\alpha(\mathbf{p})$,	molecule energy in the $\vert\alpha, \mathbf{p}\rangle$, state;
$A^{\alpha\mathbf{q}}_{\beta\mathbf{p}}$, $B^{\alpha\mathbf{q}}_{\beta\mathbf{p}}$,	Einstein coefficients of spontaneous and induced radiation per unit solid angle;
m,	molecule mass;
$f_\alpha(\mathbf{p}, \mathbf{r})$,	one-particle function of molecules distribution;
$\nu_{\alpha\beta}$,	$= (E_\alpha - E_\beta)/h$, frequency of transition;
n, j, m,	vibrational, rotational and magnetic quantum number, respectively;
k_B,	Boltzmann constant;
$N(\mathbf{r})$,	density of molecules at the $\mathbf{r}$ point;
$\mathbf{v}(\mathbf{r})$,	average local velocity of gas;
T,	transitional–rotational temperature;
T_v,	vibrational temperature;
μ,	dipole molecule moment operator;
ν, ν_0,	quantum frequency and natural frequency of diatomic molecule, respectively;
B_e,	rotational constant of a molecule;
r_e,	equilibrium internuclear distance;
ω_e,	$= \nu_0/c$, centre of vibrational–rotational band;
$\Delta\nu$,	width of vibrational–rotational band;
ε^0,	equilibrium vibrational energy per mass unit;
τ^0,	vibrational relaxation time;
ρ,	$= mN$, mass density of molecules;
$\mathbf{S}_\nu$,	spectral density of radiative flux;
$\hat{J}_\nu(\mathbf{r}_n, \mathbf{n})$,	spectral intensity of an external source radiation at the point of volume boundary in the $\mathbf{n}$ direction;
$\mathrm{d}\Omega$,	solid angle differential;
k^b_ν,	absorbtion coefficient of the condensed phase particles;
B_ν,	Plank function;
δ,	flat layer thickness;
ξ,	$= x/\delta$, dimensionless coordinate.

1. INTRODUCTION

TRANSFER of radiation in nonequilibrium gases and plasma is one of the topical subjects of modern research. This problem is connected with such engineering applications, as spectroscopy of low-temperature plasma, thermal radiation of gases at low density, molecular gas lasers. That the major portion of electromagnetic radiation in diatomic gases at temperatures of the order of several thousand degrees is transferred in the frequency ranges, corresponding to vibrational–rotational transitions, leads to an essential effect of radiation processes on population of the vibrational levels at reduced pressure of $P \sim 10^{-3}$–10^{-6} atm [1, 2].

A complete set of the kinetic equations for the dynamics of an arbitrary molecular or atomic neutral rarified gas, with allowance for radiation processes is of the form

$$\left(\frac{1}{c}\frac{\partial}{\partial t} + \mathbf{n}\nabla\right)J(\mathbf{k}) = h\omega(\mathbf{k})\sum_{\alpha\beta}\iint \mathrm{d}\mathbf{p}\,\mathrm{d}\mathbf{q}\,\delta[E_\alpha(\mathbf{q}) - E_\beta(\mathbf{p}) - \omega(\mathbf{k})]\cdot$$

$$\cdot\delta(\mathbf{q}-\mathbf{p}-\mathbf{k})\{f_\alpha(\mathbf{q},\mathbf{r})A^{\alpha\mathbf{q}}_{\beta\mathbf{p}} + J(\mathbf{k})[f_\alpha(\mathbf{q},\mathbf{r}) - f_\beta(\mathbf{p},\mathbf{r})]B^{\alpha\mathbf{q}}_{\beta\mathbf{p}}\}, \quad (1)$$

$$\left(\frac{\partial}{\partial t} + \frac{\mathbf{p}}{m}\nabla\right)f_\alpha(\mathbf{p}) \doteq \sum_{\beta\gamma\delta}\iiint |M^{\alpha\beta}_{\gamma\delta}|^2\delta(E^{\alpha\beta}_i - E^{\gamma\delta}_f)\delta(\mathbf{p}_i - \mathbf{p}_f)\cdot$$

$$\cdot\{f_\gamma(\mathbf{p}'')f_\delta(\mathbf{p}''') - f_\alpha(\mathbf{p})f_\beta(\mathbf{p}')\}\,\mathrm{d}\mathbf{p}'\,\mathrm{d}\mathbf{p}''\,\mathrm{d}\mathbf{p}''' + St_r\{f_\alpha\}, \quad (2)$$

in which $St_r\{f_\alpha(\mathbf{p}, \mathbf{r}, t)\}$ is a radiation integral of collisions

$$St_r\{f_\alpha(\mathbf{p},\mathbf{r},t)\} = \int_0^\infty \mathrm{d}\omega(\mathbf{k})\int_{(4\pi)} \mathrm{d}\Omega\,\chi_\alpha(\mathbf{p},\mathbf{k}),$$

$$\chi_\alpha(\mathbf{p},\mathbf{k}) = \sum_\gamma A_{\alpha\mathbf{p}}^{\gamma\mathbf{p}+\mathbf{k}}\delta[E_\gamma(\mathbf{p}+\mathbf{k}) - E_\alpha(\mathbf{p}) - \omega(\mathbf{k})]f_\gamma(\mathbf{p}+\mathbf{k})$$
$$- \sum_\gamma A_{\gamma\mathbf{p}-k}^{\alpha\mathbf{p}}\delta[E_\alpha(\mathbf{p}) - E_\gamma(\mathbf{p}-\mathbf{k}) - \omega(\mathbf{k})]f_\alpha(\mathbf{p})$$
$$+ \sum_\gamma B_{\alpha\mathbf{p}}^{\gamma\mathbf{p}+\mathbf{k}}\delta[E_\gamma(\mathbf{p}+\mathbf{k}) - E_\alpha(\mathbf{p}) - \omega(\mathbf{k})][f_\gamma(\mathbf{p}+\mathbf{k}) - f_\alpha(\mathbf{p})]J(\mathbf{k})$$
$$- \sum_\gamma B_{\gamma\mathbf{p}-\mathbf{k}}^{\alpha\mathbf{p}}\delta[E_\alpha(\mathbf{p}) - E_\gamma(\mathbf{p}-\mathbf{k}) - \omega(\mathbf{k})][f_\alpha(\mathbf{p}) - f_\gamma(\mathbf{p}-\mathbf{k})]J(\mathbf{k}), \qquad (3)$$

where the following notation is introduced

$$\mathbf{p}_i = \mathbf{p}+\mathbf{p}', \qquad E_i^{\alpha\beta} = E_\alpha(\mathbf{p}) + E_\beta(\mathbf{p}'),$$
$$\mathbf{p}_f = \mathbf{p}''+\mathbf{p}''', \qquad E_f^{\gamma\delta} = E_\gamma(\mathbf{p}'') + E_\delta(\mathbf{p}'''),$$
$$\sigma_{\gamma\delta}^{\alpha\beta}(\mathbf{p},\mathbf{p}') = \frac{m}{|\mathbf{p}-\mathbf{p}'|}\iint |M_{\gamma\delta}^{\alpha\beta}|^2\delta(E_i^{\alpha\beta} - E_f^{\gamma\delta})\delta(\mathbf{p}_i - \mathbf{p}_f)\,\mathrm{d}\mathbf{p}''\,\mathrm{d}\mathbf{p}'''.$$

Derivation of equations (1)–(3) from the standpoint of strict quantum statistics as well as with regard for radiation polarization, is available in the papers published by one of the authors of [3–5]. Since direct use of the kinetic equations involves substantial mathematical difficulties, it is expedient to introduce a number of simplifications, based on simple physical arguments. First, we shall use superpositional harmonic oscillator–rigid rotator approximation [6] with the aim of describing quantum properties of molecules. Besides, we shall assume that the local thermodynamic equilibrium conditions are fulfilled in vibrational and transitional-rotational degrees of freedom separately [7]. In the first part of the work, derivation of equations for a nonequilibrium radiating heteronuclear diatomic gas (e.g. CO, HCl, NO and so on) is given on the basis of the original set of equations (1)–(3) with appropriate assumptions. In the second part an outline is given of the approximated methods developed for a nonequilibrium state, and of the diffusion approximation in particular.

2. THE EQUATION OF RADIATIVE TRANSFER IN VIBRATIONAL NONEQUILIBRIUM DIATOMIC GAS

Using the above assumption that the local thermodynamic equilibrium takes place inside separate degrees of freedom, we arrive at the factorized function of distribution

$$f_\alpha(\mathbf{p},\mathbf{r}) = N(\mathbf{r})N(\mathbf{p})N_v(n)N_r(j,m), \qquad (4)$$

in which

$$N(\mathbf{p}) = (2\pi m k_B T)^{-3/2}\exp\left\{-\frac{[\mathbf{p} - m\mathbf{v}(\mathbf{r})]^2}{2mk_B T}\right\}, \qquad (5)$$

$$N_v(n) = Q_v^{-1}\exp\left(-\frac{E_n}{k_B T}\right), \qquad Q_v(T_v) = \sum_{n=0}^{\infty}\exp\left\{-\frac{(n+\frac{1}{2})h\nu_0}{k_B T_v}\right\}, \qquad (6)$$

$$N_r(j,m) = Q_r^{-1}\exp\left(-\frac{E_j}{k_B T}\right), \qquad Q_r(T) = \sum_{j=0}^{\infty}(2j+1)\exp\left\{-\frac{j(j+1)hcB_e}{k_B T}\right\}. \qquad (7)$$

This leads automatically to correct normalization for one-particle distribution function

$$\sum_\alpha\int f_\alpha(\mathbf{p},\mathbf{r},t)\,\mathrm{d}\mathbf{p} = N(\mathbf{r},t), \qquad (8)$$

where $\alpha = (n,j,m)$, $m = 0, \pm 1 \pm 2 \pm \ldots \pm j$.

Integrating equation (1) with respect to a momentum and taking account of (4, 5) gives

$$\left(\frac{1}{c}\frac{\partial}{\partial t} + \mathbf{n}\nabla\right)J(\mathbf{k}) = \omega(\mathbf{k})N(\mathbf{r})\sum_{\alpha\beta}\phi_\beta^\alpha(\nu)\{N_\alpha A_\beta^\alpha + J(\mathbf{k})(N_\alpha - N_\beta)B_\beta^\alpha\}, \qquad (9)$$

in which $N_\alpha(\mathbf{r}) = N(\mathbf{r})N_v(n)N_r(j,m)$,

$$\phi_\beta^\alpha(\nu) = \left(\frac{mc^2}{2\pi k_B T\nu_{\alpha\beta}^2}\right)^{1/2}\exp\left\{-\frac{mc^2}{2k_B T\nu_{\alpha\beta}^2}(\nu - \nu_{\alpha\beta})^2\right\}. \qquad (10)$$

Summation over the magnetic quantum numbers of (9) yields the equation

$$\left(\frac{1}{c}\frac{\partial}{\partial t} + \mathbf{n}\nabla\right)J(\mathbf{k}) = \omega(\mathbf{k})N(\mathbf{r})\sum_{nn'jj'}\phi_{n'j'}^{nj}(\nu)\{q(j')N_v(n)N_r(j)A_{n'j'}^{nj}$$
$$+ J(\mathbf{k})[q(j')N_v(n)N_r(j) - q(j)N_v(n')N_r(j')]B_{n'j'}^{nj}\} \qquad (11)$$

in which

$$N_r(j) = \sum_{m=-j}^{j} N_r(j, m) = Q_r^{-1} q(j) \exp\left\{ -\frac{E_j}{k_B T} \right\}, \tag{12}$$

$q(j) = (2j+1)$ is the level degeneration multiplicity with the fixed rotational quantum number. In dipole approximation

$$B_{n'j'}^{nj} = \frac{2\pi}{3\hbar^2 c} q^{-1}(j) q^{-1}(j') \sum_{mm'} |\langle njm|\boldsymbol{\mu}|n'j'm'\rangle|^2. \tag{13}$$

Calculation of the square of a matrix element of diatomic molecule dipole moment yields the following expression in superpositional approximation [6]

$$\sum_{mm'} |\langle njm|\boldsymbol{\mu}|n'j'm'\rangle|^2 = \frac{nB_e r_e^2}{\omega_e} \delta_{n'+1}^{n} [j\delta_{j-1}^{j'} + (j+1)\delta_{j+1}^{j'}] \left(\frac{\partial \mu}{\partial r}\right)_{r=r_e}^2 . \tag{14}$$

With the use of (14) and the new notation

$$\phi_{j'}^{j}(\nu) \equiv \phi_{n-1j'}^{nj}(\nu), \qquad B = \frac{2\pi}{3\hbar^2 c} \frac{B_e r_e^2}{\omega_e} \left(\frac{\partial \mu}{\partial r}\right)_{r=r_e}^2, \tag{15}$$

summation can be made in (11) over the vibrational quantum numbers

$$\left(\frac{1}{c}\frac{\partial}{\partial t} + \mathbf{n}\nabla\right) J(\mathbf{k}) = \frac{N(\mathbf{r})h\nu B}{\exp\left(\frac{h\nu_0}{k_B T_v}\right) - 1} \sum_{jj'} Q_r^{-1}(T) \exp\left(-\frac{E_j}{k_B T}\right) \phi_{j'}^{j}(\nu)$$

$$\cdot [j\delta_{j-1}^{j'} + (j+1)\delta_{j+1}^{j'}] \left\{ \frac{2h\nu^3}{c^2} - J(\mathbf{k}) \left[\exp\left(\frac{h\nu_0}{k_B T_v} + \frac{E_j - E_{j'}}{k_B T} \right) - 1 \right] \right\}. \tag{16}$$

Further transformations are connected with the use of the evident correlation

$$\phi_{j\pm 1}^{j}(\nu) \left[\exp\left(\frac{h\nu_0}{k_B T_v} + \frac{E_j - E_{j\pm 1}}{k_B T} \right) - 1 \right] \simeq \phi_{j\pm 1}^{j}(\nu) \left[\exp\left(\frac{h\nu_0}{k_B T_v} + \frac{h(\nu - \nu_0)}{k_B T} \right) - 1 \right], \tag{17}$$

high accuracy of which is ensured by a delta-shaped character of the line-shape function (10). Having made summation in (16) over the rotational quantum number j' and taken into account (17), we obtain the radiative transfer equation

$$\left(\frac{1}{c}\frac{\partial}{\partial t} + \mathbf{n}\nabla\right) J(\mathbf{k}) = \kappa_\nu (N, T_v, T)(B_\nu (T_v, T) - J(\mathbf{k})), \tag{18}$$

in which

$$B_\nu (T_v, T) = \frac{2h\nu^3}{c^2} \left\{ \exp\left[\frac{h\nu_0}{k_B T_v} + \frac{h(\nu - \nu_0)}{k_B T} \right] - 1 \right\}^{-1}, \tag{19}$$

$$\kappa_\nu (N, T_v, T) = N(\mathbf{r}) h\nu B \left(\frac{\nu}{\nu_0}\right)^3 B_{\nu_0}(T_v, T) B_\nu^{-1}(T_v, T)$$

$$\cdot \sum_{j=0}^{\infty} Q_r^{-1} \exp\left(-\frac{E_j}{k_B T} \right) [(j+1)\phi_{j+1}^{j}(\nu) + j\phi_{j-1}^{j}(\nu)]. \tag{20}$$

In the majority of cases the following inequality holds

$$\nu_0/T_v \gg \Delta\nu/T, \tag{21}$$

which yields an extremely simple form of the transfer equation

$$\left(\frac{1}{c}\frac{\partial}{\partial t} + \mathbf{n}\nabla\right) J(\mathbf{k}) = k_\nu (N, T)[J_\nu^0(T_v) - J(\mathbf{k})], \tag{22}$$

where

$$J_\nu^0(T_v) = \frac{2h\nu^3}{c^2} \left[\exp\left(\frac{h\nu_0}{k_B T_v} \right) - 1 \right]^{-1}, \tag{23}$$

$$k_\nu (N, T) = h\nu NB \sum_{j=0}^{\infty} \sum_{\alpha=0}^{1} S_{j\alpha} \phi_{j\alpha}(\nu), \tag{24}$$

$$S_{j\alpha} = (j+\alpha)\frac{hcB_e}{k_B T}\exp\left\{-j(j+1)\frac{hcB_e}{k_B T}\right\}. \tag{25}$$

$$\phi_{j\alpha}(\nu) = \pi^{-1/2}\gamma_{j\alpha}^{-1}\exp\left[-\frac{(\nu-\nu_{j\alpha})^2}{\gamma_{j\alpha}^2}\right]. \tag{26}$$

$$\gamma_{j\alpha} = \nu_{j\alpha}\left(\frac{2k_B T}{mc^2}\right)^{1/2}. \qquad \nu_{j\alpha} = \nu_0 + 2(1-2\alpha)(j+\alpha)cB_e. \tag{27}$$

Here $S_{j\alpha}$ is the line strength, $\nu_{j\alpha}$ the centre, $\gamma_{j\alpha}$ the half-width and $\phi_{j\alpha}(\nu)$ the line-shape function of an appropriate spectral line, with $\alpha = 0$ corresponding to the P-branch, and $\alpha = 1$, to the R-branch. In this case, as may be readily verified, the following normalization conditions are satisfied

$$\sum_{j=0}^{\infty}\sum_{\alpha=0}^{1} S_{j\alpha} = 1, \qquad \int_{-\infty}^{\infty}\phi_{j\alpha}(\nu)\,\mathrm{d}\nu = 1. \tag{28}$$

Note that in formula (25) a well-known value of the rotational partition function was used, which holds at $k_B T \gg hcB_e$

$$Q_r(T) \simeq \int_0^{\infty}(2j+1)\exp\left\{-j(j+1)\frac{hcB_e}{k_B T}\right\}\mathrm{d}j = \frac{k_B T}{hcB_e}. \tag{29}$$

For calculation of the Einstein coefficient of induced radiation, it is necessary to know the constant $(\partial\mu/\partial r)_{r=r_e}$, which for the molecules HCl, HBr, NO, CO is in linear relationship with E/r_e^2 [8]. Here E is the energy of dissociation. For the molecules of CO, this, for example, leads to the value $B = 7.03 \cdot 10^5$ sm^2/erg · s, which agrees well with the measured integral absorption coefficient in the main CO band [6].

Note that equation (23) was phenomenologically developed in [9], and that equation (18) is distinguished by somewhat different definition of the absorption coefficient than that given in [10].

3. DERIVATION OF THE MASTER INTEGRAL EQUATION FOR THE DENSITY OF VIBRATIONAL ENERGY OF A DIATOMIC GAS

Kinetic equation (2) for the nonequilibrium state of a diatomic gas can be considerably simplified by using the above assumptions. Let equation (2) be integrated with respect to the momentum and then summation made over the rotational, j, and magnetic, m, numbers taking into account (4)–(7). Rather cumbersome transformations yield the equation for the occupation numbers $N(n) = N(\mathbf{r})N_r(n)$ of the vibrational levels

$$\frac{\partial}{\partial t}N(n) + \nabla(\mathbf{v}(\mathbf{r})N(n)) = \sum_{\substack{k \\ (k\neq n)}}(N(k)R_{kn} - N(n)R_{nk}) + \sum_{j=0}^{\infty}\sum_{m=-j}^{j}\int \mathrm{d}\mathbf{p}St_r\{f_{njm}(\mathbf{p},\mathbf{r},t)\}. \tag{30}$$

Here the elements of the matrix of transition probabilities R_{kn} at $n > k$ are determined by

$$R_{kn} = \frac{\pi N(\mathbf{r})}{2}\left(\frac{m}{\pi k_B T}\right)^{3/2}\int_0^{\infty}\sigma_{kn}(u)u^3\exp\left(-\frac{mu^2}{4k_B T}\right)\mathrm{d}u, \tag{31}$$

where $\sigma_{kn}(u)$ is the cross-section of exitation of transition, induced by nonelastic collisions with a relative velocity u. In approximation of a harmonic oscillator, the probability of transition inside the vibrational degrees of freedom, at non-elastic collisions, is proportional to the upper level quantum number [7], whence

$$R_{nk} = n\delta^n_{k+1}R_{10} + (n+1)\delta^n_{k-1}R_{01}. \tag{32}$$

Multiplying equation (30) by $nh\nu_0$ and summating over it from 0 ad infinitum, allowing for (32), one obtains

$$\frac{\partial}{\partial t}E_r + \nabla(\mathbf{v}E_r) = \frac{E_r^0 - E_r}{\tau^0} + \sum_{n=0}^{\infty}\sum_{j=0}^{\infty}\sum_{m=-j}^{j} nh\nu_0\int \mathrm{d}\mathbf{p}St_r\{f_{njm}\}, \tag{33}$$

in which

$$E_r = \sum_{n=0}^{\infty}E_n N(n) - \tfrac{1}{2}h\nu_0 N(\mathbf{r}), \tag{34}$$

$$E_r^0 = Nh\nu_0\left[\exp\left(\frac{h\nu_0}{k_B T}\right) - 1\right]^{-1}. \qquad \tau^0 = R_{10}^{-1}\left[1 - \exp\left(-\frac{h\nu_0}{k_B T}\right)\right]^{-1}. \tag{35}$$

The transform of the collision radiative integral of equation (33) is accomplished as follows. Using the definition $\chi_\alpha(\mathbf{p},\mathbf{k})$ (3) and neglecting the momentum transfer between a photon and a molecule during absorption and radiation, one can easily see that

$$\sum_{\alpha}\int \mathrm{d}\mathbf{p}E_{\alpha}(\mathbf{p})\chi_{\alpha}(\mathbf{p},\mathbf{k}) = -\sum_{\alpha\gamma}\int \mathrm{d}\mathbf{p}\delta[E_{\alpha}(\mathbf{p})-E_{\gamma}(\mathbf{p})-\omega(\mathbf{k})]$$

$$\cdot[E_{\alpha}(\mathbf{p})-E_{\gamma}(\mathbf{p})]\{A^{\alpha}_{\gamma}f_{\alpha}(\mathbf{p})+B^{\alpha}_{\gamma}[f_{\alpha}(\mathbf{p})-f_{\gamma}(\mathbf{p})]J(\mathbf{k})\}. \tag{36}$$

Using the equation of radiative transfer (1), where the term $(1/c)(\partial/\partial t)J(\mathbf{k})$ can obviously be neglected, equation (36) may be written as

$$h\sum_{\alpha}\int \mathrm{d}\mathbf{p}E_{\alpha}(\mathbf{p})\chi_{\alpha}(\mathbf{p},\mathbf{k}) = -\mathbf{n}\nabla J(\mathbf{k}), \tag{37}$$

whence, according to (3)

$$\sum_{\alpha}\int \mathrm{d}\mathbf{p}E_{\alpha}(\mathbf{p})St_{r}\{f_{\alpha}(\mathbf{p},\mathbf{r},t)\} = -\nabla\int_{0}^{\infty}\mathbf{S}_{\nu}\,\mathrm{d}\nu. \tag{38}$$

It is obvious now that by transformations similar to (36)–(38), provided that

$$\nu_0 \gg \Delta\nu \tag{39}$$

equation (33) can be presented as

$$\left(\frac{\partial}{\partial t}+\mathbf{v}\nabla\right)\varepsilon = \frac{\varepsilon^{0}-\varepsilon}{\tau^{0}}-\frac{1}{\rho}\nabla\int \mathbf{S}_{\nu}\,\mathrm{d}\nu, \tag{40}$$

with mean vibrational energy per unit mass $\varepsilon = E_{v}/\rho$ being introduced for convenience. In derivation of (40), the equation of continuity $(\partial/\partial t)\rho+\nabla(\mathbf{v}\rho) = 0$ has been used. Phenomenologically equation (40) was derived in [10]. From the given approach it follows that for derivation of (40) it is indispensible that condition (39) should be satisfied, which is really the case. To exclude from (40) the unknown value—radiative flux density—we shall integrate the transfer equation (22) with respect to the solid angle

$$\nabla\mathbf{S}_{\nu} = 4\pi q\nu^{3}k_{\nu}\,\varepsilon-k_{\nu}\int_{(4\pi)}J(\mathbf{k})\,\mathrm{d}\Omega, \tag{41}$$

in which

$$J(\mathbf{k}) = \int k_{\nu}J^{0}_{\nu}\exp[-\tau_{\nu}(\mathbf{r},\mathbf{r}')]\,\mathrm{d}s'+\hat{J}_{\nu}\exp[-\tau_{\nu}(\mathbf{r},\mathbf{r}_{n})], \tag{42}$$

$$q = \frac{2m}{c^{2}\nu_{0}},\qquad \tau_{\nu}(\mathbf{r},\mathbf{r}') = \int_{0}^{|\mathbf{r}-\mathbf{r}'|}k_{\nu}(s)\,\mathrm{d}s. \tag{43}$$

where $\hat{J}_{\nu}(\mathbf{r}_{n},\mathbf{n})$ is the intensity of external radiation. Simultaneously, by definition of (34)

$$\varepsilon = m^{-1}\left[\sum_{n=0}^{\infty}\frac{E_{n}}{Q_{v}}\exp\left(-\frac{E_{n}}{k_{B}T_{v}}\right)-E_{0}\right] = \frac{h\nu_{0}}{m}\left[\exp\left(\frac{h\nu_{0}}{k_{B}T_{v}}\right)-1\right]^{-1}, \tag{44}$$

whence in the approximation (21) one obtains the linear relationship

$$J^{0}_{\nu}(\mathbf{r},t) = q\nu^{3}\varepsilon(\mathbf{r},t). \tag{45}$$

Substitution of (41) into the right-hand side of equation (40) and exclusion of $J(\mathbf{k})$ and J^{0}_{ν} respectively with the help of (42) and (45), yields the integrodifferential equation for the density distribution of vibrational energy [5, 11, 12]

$$\left(\frac{\partial}{\partial t}+\mathbf{v}\nabla+\frac{1}{\tau}\right)\varepsilon(\mathbf{r},t) = \int_{V}G(\mathbf{r},\mathbf{r}')\varepsilon(\mathbf{r}',t)\,\mathrm{d}\mathbf{r}'+\frac{\varepsilon^{0}(\mathbf{r},t)}{\tau^{0}}+\psi(\mathbf{r},t), \tag{46}$$

where

$$G(\mathbf{r},\mathbf{r}') = \frac{q}{\rho(\mathbf{r})}\int_{\Delta\nu}\nu^{3}k_{\nu}(\mathbf{r})k_{\nu}(\mathbf{r}')\frac{\exp[-\tau_{\nu}(\mathbf{r},\mathbf{r}')]}{|\mathbf{r}-\mathbf{r}'|^{2}}\,\mathrm{d}\nu, \tag{47}$$

$$\psi(\mathbf{r},t) = \frac{1}{\rho(\mathbf{r})}\int_{\Delta\nu}\mathrm{d}\nu\int_{(4\pi)}\mathrm{d}\Omega k_{\nu}(\mathbf{r})\hat{J}_{\nu}(\mathbf{r}_{n},\mathbf{n})\exp[-\tau_{\nu}(\mathbf{r},\mathbf{r}_{n})], \tag{48}$$

$$\frac{1}{\tau(\mathbf{r},t)} = \frac{1}{\tau^{0}(\mathbf{r},t)}+\frac{1}{\tau^{*}},\qquad \frac{1}{\tau^{*}} = \frac{4\pi q}{\rho}\int_{\Delta\nu}\nu^{3}k_{\nu}\,\mathrm{d}\nu. \tag{49}$$

Equation (46) together with the equations of conservation of mass, momentum and energy, form a closed set of equations for the dynamics of a nonequilibrium relaxing radiating diatomic gas. Now, to determine the radiation field, it is sufficient to use equations (42, 45).

Now we shall calculate the radiation time τ^*. Substituting (24) into equation (49) and using normalization conditions (28) in the approximation (39), one obtains

$$\frac{1}{\tau^*} = \frac{8\pi h B}{c^2 \nu_0} \sum_{j\alpha} S_{j\alpha} \nu_{j\alpha}^4 \simeq \frac{8\pi h B \nu_0^3}{c^2}. \tag{50}$$

By using the equation, relating the Einstein coefficients for the induced and spontaneous radiation. we determine $1/\tau^* = 4\pi A$, where A is the coefficient of spontaneous radiation per unit of a solid angle.

It should be noted in conclusion, that, as derivation of equation (46) requires the fulfilment of conditions (21, 39), at sufficiently high vibrational temperature $T_v \gg T$, condition (21) is violated and equation (46) becomes inapplicable. It can be readily seen, that in this case an equation similar to (46) can still be obtained, which, though, will be nonlinear, since the function $B_\nu(T_v, T)$ (19) is not proportional to $\varepsilon(\mathbf{r})$ (44), as was the case with (45). Besides, additional nonlinearity appears, because of the absorption coefficient $\kappa_\nu(N, T_v, T)$ (20) depending also on T_v. Such generalization of equation (46) being trivial, it will not be presented here.

REFERENCES

1. Ya. B. Zeldovich and Yu. P. Raizer, *Physics of Shock Waves and High-Temperature Hydrodynamic Phenomena*, pp. 260–264. Nauka, Moscow (1966).
2. S.-I Pai, *Radiation Gas Dynamics*, p. 298. Mir, Moscow (1968).
3. V. I. Kruglov, Synopsis of the paper for the Second International Conference on the Theory of Plasma, Kiev, 17 (1976).
4. V. I. Kruglov, Equation of the tensor of radiation intensity of a nonequilibrium gas, *Dokl. Akad. Nauk. BSSR* **19**, 212–215 (1975).
5. V. I. Kruglov, To the theory of vibrational nonequilibrium radiation of diatomic gases, thesis, Minsk, 12–47 (1975).
6. S. S. Penner, Quantitative molecular spectroscopy and gas emissivities, California Institute of Technology (1963).
7. J. F. Clarke and M. McChesney, *The Dynamics of Real Gases*. Butterworths, London (1964).
8. T. Sue-Sen, *Physical Mechanics*, p. 518. Mir, Moscow (1965).
9. R. M. Goody, *Atmospheric Radiation*. Oxford University Press, Oxford (1964).
10. S. E. Gilles and W. C. Vincenti, Coupled radiative and vibrational nonequilibrium in a diatomic gas, with application to gas dynamics, *J. Quantve Spectrosc. Radiat. Transfer* **10**, 71–97 (1970).
11. V. I. Kruglov and Yu. V. Khodyko, Integral equation for the vibrational energy density of diatomic gases, *Dokl. Akad. Nauk. BSSR*, **19**, 510–513 (1975).
12. M. A. Elyashevich, V. I. Kruglov and Yu. V. Khodyko, Derivation of the Biberman–Holstein type equation for nonequilibrium radiative diatomic gas, *Pis'ma Zh. Eksp. Teor. Fiz.* **20**, 95–97 (1974).

RAYONNEMENT DANS LES GAZ DIATOMIQUES EN NON-EQUILIBRE DE VIBRATION—I

Résumé—Dans la première partie on obtient les équations macroscopiques pour le champ radiatif et l'état interne d'un gaz diatomique en déséquilibre de vibration, à l'aide d'un système d'équations cinétiques pour l'intensité spectrale et la fonction de distribution des molécules. En outre, pour la distribution d'énergie de vibration, l'équation fondamentale intégro-différentielle est obtenue, laquelle forme un système complet avec les équations de bilan de quantité de mouvement, de masse et d'énergie.

VIBRATIONS-UNGLEICHGEWICHTS-STRAHLUNG VON ZWEIATOMIGEN GASEN, TEIL I

Zusammenfassung—Mit Hilfe der kinetischen Gleichung für spektrale Strahlungsintensität und der Verteilungsfunktion für Einpartikel im Molekül, wurde im 1. Teil die makroskopische Gleichung für das Strahlungsfeld und den inneren Zustand schwingender nicht gleichgewichtiger zweiatomiger Gase hergeleitet. Außerdem wird die Lösung der Grund-Integral-Differentialgleichung für die Schwingungsenergieverteilung hergeleitet, welche zusammen mit den Impuls-, Massen- und Energieerhaltungssätzen ein geschlossenes System bildet.

КОЛЕБАТЕЛЬНО-НЕРАВНОВЕСНОЕ ИЗЛУЧЕНИЕ ДВУХАТОМНЫХ ГАЗОВ. ЧАСТЬ 1.

Аннотация — В первой части с помощью системы кинетических уравнений для спектральной интенсивности излучения и одночастичной функции распределения молекул получены макроскопические уравнения, описывающие поле излучения и внутреннее состояние колебательно-неравновесного двухатомного газа. Кроме того дан вывод основного интегро-дифференциального уравнения для распределения колебательной энергии, которое в совокупности с уравнениями сохранения массы импульса и энергии образуют замкнутую систему.