QUESTION OF DETERMINING THE RELAXATION TIME IN KINETIC COOLING OF A MOVING GAS

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Absorption of resonance radiation by a gas can result in diminution of its translational temperature [1, 2]. This effect was experimentally recorded in the absorption of laser radiation of wavelength λ = 10.6 μm in gases containing CO_2 molecules [3, 4]. The lifetime of the kinetic cooling effect under impulse action on a medium is determined substantially by the time of the vibrational–vibrational (V–V') relaxation of the upper level of the absorption transition (00°1 for CO_2) and the cooling depth by the time of vibrational–translational (V–T) relaxation of the lower level (10°0). Hence, the V–T relaxation time [4] can be judged by the depth of cooling.

The effect of continuous resonance radiation on a medium moving with a given velocity can also result in a change in the translational temperature and in other macroscopic flow parameters, as will be shown below. In this paper the possibility of determining the characteristic times of both V–T and intramolecular and intermolecular V–V processes by the change in the gasdynamic stream parameters in the radiation action zone is investigated.

Motion of a medium in the presence of a radiation field whose intensity does not change with time (I = const) will be considered in the inviscid, non-heat-conducting gas approximation. We shall also assume that the rotational temperature, and a local thermodynamic equilibrium with a certain vibrational temperature exists in each type of vibration modeled by a harmonic oscillator.

The equations of motion of such a medium in a constant section channel have the following normal form:

$$\frac{dT}{dx} = \frac{1 - \varkappa M_a^2}{(1 - M_a^2) C_p} J, \quad \frac{du}{dx} = \frac{(\varkappa - 1) M_a^2}{(1 - M_a^2) u} J,$$

$$\frac{dp}{dx} = -\frac{\rho (\varkappa - 1) M_a^2}{(1 - M_a^2)} J, \quad \frac{d\rho}{dx} = -\frac{\varkappa p (\varkappa - 1)}{(1 - M_a^2)} J,$$

$$J = \frac{k_v I}{\rho u} - \sum_{i=1}^{M} \frac{de_V^i}{dx}, \quad C_p = \frac{R}{\mu} \left(\frac{5}{2} + \sum_{i=1}^{L} \gamma_i + \frac{3}{2} \sum_{i=L+1}^{M} \gamma_i \right),$$

$$\varkappa = 1 + \left(\frac{3}{2} + \sum_{i=1}^{L} \gamma_i + \frac{3}{2} \sum_{i=L+1}^{M} \gamma_i \right)^{-1}, \quad M_a = \frac{u}{\sqrt{\varkappa \frac{R}{\mu} T}}, \quad e_V^i = \gamma_i \sum_{j=1}^{n} \frac{\Theta_{ij} R}{\mu} \varepsilon_j,$$

(1)

where ρ, p, T, u are the density, pressure, translational temperature, and gas velocity; μ, molecular weight of the mixture; k_v, spectral absorptive index; γ_i, molar fraction of the i-th component in the mixture; M, total number of molecular components in the mixture; L, their number of linear rigid molecules; n, number of vibrations types in the i-th component; $\varepsilon_j = g_j [\exp(\Theta_j/T_j) - 1]^{-1}$; Θ_j and T_j, characteristic and local vibrational temperatures in the j-th type of vibration; and g_j, multiplicity of its degeneration.

Let us consider the flow of a binary mixture, one of whose components is molecules possessing at least two types of vibrations q and s, with dissimilar relaxation times and unrelated resonance, while the other is molecules, one of whose types of vibrations p is related to the fast nonresonant V–V' exchange with mode s, while the remaining types of vibrations are slowly relaxing. Let the radiation frequency also be $v_{mn} = (n\Theta_s - m\Theta_q)/h$ (n and m are the numbers of the upper and lower vibrational levels of the absorbing transition that belong to the modes s and q, respectively). In this case the system of kinetic equations can be represented in the form

$$\frac{d\varepsilon_q}{dx} = \frac{p}{kT}\left[-l_q\frac{\mu^2 k_\nu I}{\rho^2 N_A^2 h\nu_{mn}\gamma_k}\right.$$

$$\left.-(\varepsilon_q-\varepsilon_{q0})\sum_{i=1}^{M}W_{q0}^i\gamma_i+\frac{l_q}{g_q}L_{qs}\sum_{i=1}^{M}W_{qs}^i\gamma_i\right]; \tag{2}$$

$$\frac{d\varepsilon_s}{dx} = \frac{p}{kT}\left[l_s\frac{\mu^2 k_\nu I}{\rho^2 N_A^2 h\nu_{mn}\gamma_k}-\frac{l_s}{g_s}L_{qs}\sum_{i=1}^{M}W_{qs}^i\gamma_i+\frac{l_s}{g_s}L_{sp}W_{sp}\gamma_p\right]; \tag{3}$$

$$\frac{d\varepsilon_p}{dx} = \frac{p}{kT}\left[-\frac{l_p}{g_p}L_{sp}W_{sp}\gamma_k\right], \tag{4}$$

$$L_{sp} = \left[\varepsilon_p^{l_p}(\varepsilon_s+1)^{l_s}\exp\left(\frac{\Theta_p-\Theta_s}{T}\right)-(\varepsilon_p+1)^{l_p}\varepsilon_s^{l_s}\right],$$

where W_{qs}^i is the velocity of the intramolecular V–V' exchange between the modes q and s during collisions with the i-th partner; W_{sp}, velocity of the intermolecular V–V' exchange between the modes s and p; l_s, l_q, and l_p, quantity of vibrational quanta lost by the modes s and p acquired by the mode q during the V–V' exchange; W_{q0}^i, velocity of V–T relaxation for the mode q during collisions with the i-th partner; h, Planck constant; N_A, Avogadro number; ν_{mn}, frequency of the absorbing transition at the center of the spectrum line; γ_k and γ_p, molar fractions of the absorbing component and the component containing a vibration of the type p; and k, Boltzmann constant.

Taking account of (2)–(4), the expression for J can be represented in the form

$$J = \frac{Rp\Theta_q}{\mu kTu}\gamma_k\sum_{i=1}^{M}W_{q0}^i\gamma_i\left[\varepsilon_q-\varepsilon_{q0}+L_{qs}\left(\frac{l_s}{g_s}\frac{\Theta_s}{\Theta_q}-\frac{l_q}{g_q}\right)\sum_{i=1}^{M}\frac{W_{qs}^i}{W_{q0}^i}\gamma_i+L_{sp}\frac{\Theta_p}{\Theta_q}\frac{W_{sp}\gamma_p}{\sum_{i=1}^{M}W_{q0}^i\gamma_i}\left(\frac{l_p}{g_p}-\frac{\Theta_s}{\Theta_p}\frac{l_s}{g_s}\right)\right]. \tag{5}$$

If J < 0, then for $0 < M_a < 1/\sqrt{\varkappa}$ the gas will be cooled and retarded (dT/dx < 0, du/dx < 0, d_ρ/dx > 0, dp/dx > 0), for $1/\sqrt{\varkappa} < M_a < 1$ it is heated and retarded (dT/dx > 0, du/dx < 0, d /dx > 0, dp/dx > 0), and for M_a > 1 it is cooled and accelerated (dT/dx < 0, du/dx > 0, d /dx < 0, dp/dx < 0). If J > 0, then for $0 < M_a < 1/\sqrt{\varkappa}$ dT/dx > 0, du/dx > 0, d_ρ/dx < 0, dp/dx < 0, for $1/\sqrt{\varkappa} < M_a < 1$ dT/dx < 0, du/dx > 0, d_ρ/dx < 0, dp/dx < 0, and for M_a > 1, DT/dx > 0, du/dx < 0, d_ρ/dx > 0, dp/dx > 0. For J = 0 the gasdynamic parameters in the absorption zone will not vary.

The considered regularities in the change in macroscopic parameters permit determination of the relaxation time for V–T and V–V' processes in the mixture under consideration during absorption of constant intensity resonance radiation.

Indeed, let a gas consisting of just the absorbing component (γ_k = 1), $\varepsilon_j = \varepsilon_{j_0}$ (j = q, s) and $\tau_{V-T}^{q0} < \tau_{V-V'}^{qs}$ (τ_{V-T}^{q0} и $\tau_{V-V'}^{qs}$ are the characteristic times of the V–T and the intramolecular V–V' exchanges) first flow along a channel of constant section. For definiteness we assume that $0 < M_a < 1/\sqrt{\varkappa}$. In this case $d\varepsilon_q$/dx < 0, because of the induced transitions of molecules with level m to the level n, and as a result of the energy exchange between the translational chaotic motion of molecules of the mixture and the mode q an energy flux occurs from the translational to the vibrational degrees of freedom, i.e., J < 0. If $\tau_{V-V'}^{qs}$ = ∞, then for a given intensity I the change in the gasdynamic parameters in the absorption zone would occur to x = l_*, where l_* corresponds to the section in which

$$I = \frac{|\varepsilon_{q0}-\varepsilon_q|W_{q0}^h\gamma_k}{\mu^2 k_\nu}\rho^2 N_A^2 h\nu_{mn}\gamma_k. \tag{6}$$

is satisfied. For x > l_* saturation of the absorbing transition sets in ($y_n = y_m = \frac{y_n^0+y_m^0}{2}$,

where y_n and y_m are the relative populations of the levels n and m, and y_n^0 and y_m^0 are their equilibrium values). Therefore, by changing the magnitude of the intensity, the length of the band of variation of the macroscopic stream parameters (p, T, ρ, u) can be diminished or

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enlarged. Since I is single-valuedly connected with W_{qo}^k by relationship (6), then by means of the quantity l_* the time (τ_{V-T}^{qo}) of V—T relaxation can be judged $(W = kT/p\tau)$. By increasing the radiation intensity, the condition $l_* < l_{V-V'}^{qs}\left(l_{V-V'}^{qs} = \tau_{V-V'}^{qs}\int_0^{l_*} u\,dx/l_*\right)$ can always be be achieved.

For $x > l_{V-V'}^{qs}$, a flux of vibrational quanta from the mode s to the mode q, appears whose magnitude for $\varepsilon_q > \varepsilon_{q0} - L_{qs}\left(\dfrac{\Theta_s}{\Theta_q}\dfrac{l_s}{g_s} - \dfrac{l_q}{g_q}\right)\dfrac{W_{sq}^k}{W_{q0}^k}\gamma_k\,(L_{qs}>0)$ is greater than the flux of vibrational quanta from the mode q to the mode s because of the induced transitions.

Hence J > 0 and the sign of the derivatives dT/dx, dp/dx, du/dx, $d\rho/dx$ changes to the opposite. Hence, by the change in the experimentally measured profiles of T, p, ρ, u or their derivatives in the absorption zone, the intramolecular V—V' exchange time $\tau_{V-V'}^{sq}$, can be judged.

The situation is complicated somewhat when an impurity gas is present in the mixture.

Let $\tau_{V-T}^{q0} < \tau_{V-V'}^{ps}$, and moreover $\left(\dfrac{l_p}{g_p} - \dfrac{\Theta_s}{\Theta_p}\dfrac{l_s}{g_s}\right) < 0$, in this case the flux of vibrational quanta from the mode s to the mode p cancels the increase ε_q because of the intramolecular V—V' exchange. If the equality

$$\varepsilon_q = \varepsilon_{q0} + L_{sp}\frac{\Theta_p}{\Theta_q}\frac{W_{sp}\gamma_p}{\sum\limits_{i=1}^{M} W_{q0}^i\gamma_i}\left(\frac{l_p}{g_p} - \frac{\Theta_s}{\Theta_p}\frac{l_s}{g_s}\right) + L_{qs}\sum_{i=1}^{M}\frac{W_{qs}^i\gamma_i}{W_{q0}^i}\left(\frac{l_s}{g_s}\frac{\Theta_s}{\Theta_q} - \frac{l_q}{g_q}\right),$$

is satisfied here, and $L_{sp} > 0$ and $L_{qs} > 0$, then J = 0 and no change will occur in the macroscopic parameters for $x > l_*$, and a situation can even occur when $\varepsilon_q < \varepsilon_{q0} + L_{sp}$.

$\dfrac{\Theta_p}{\Theta_q}\dfrac{W_{sp}\gamma_p}{\sum\limits_{i=1}^{M} W_{q0}^i\gamma_i}\left(\dfrac{l_p}{g_p} - \dfrac{l_s}{g_s}\dfrac{\Theta_s}{\Theta_p}\right) + L_{qs}\sum\limits_{i=1}^{M}\dfrac{W_{qs}^i\gamma_i}{W_{q0}^i\gamma_i}\left(\dfrac{l_s}{g_s}\dfrac{\Theta_s}{\Theta_q} - \dfrac{l_q}{g_q}\right)$ and the gas in the zone of radiation action will be equally cooled and retarded despite the energy flux to the mode q due to the intramolecular V—V' exchange.

If $\left(\dfrac{l_p}{g_p} - \dfrac{l_s\Theta_s}{g_s\Theta_p}\right) > 0$, then for $L_{sp} > 0$ and $L_{qs} > 0$ the flux of vibrational quanta to the mode q grows, hence J > 0 and $|J|$ is greater than the corresponding value of $|J|$ for the action of just one intramolecular V—V' exchange between the modes q and s.

Therefore, the introduction of an impurity gas whose molecules possess vibrations of type p into the stream permits changing the nature of the radiation action on the stream, and therefore, changing the law of macroscopic parameter variation in the absorption zone. Comparing the experimental T, p, ρ, u profiles in the absorption zone for a gas flow consisting only of molecules of the absorbing component and for a mixture also containing impurity gas molecules $(\gamma_p \neq 0)$ for known values of W_{qo}^i, W_{qs}^i, Θ_s and Θ_p, we can determine the quantity W_{ps} and the time of intermolecular V—V' exchange between the modes p and s.

Now, let us examine the conditions under which the maximal gradients of the macroscopic parameters are realized in the absorption zone, and which are optimal for measuring the T, p, ρ, u profiles in the radiation action zone. Linearizing the equations of system (1) with respect to the parameter $\delta = \sum\limits_{i=1}^{M} l_V^i/H$ (this parameter was first introduced in [5]), where H is the total enthalpy of the gas, permits obtaining the following solutions for the relative change in the macroscopic parameters in the absorption zone:
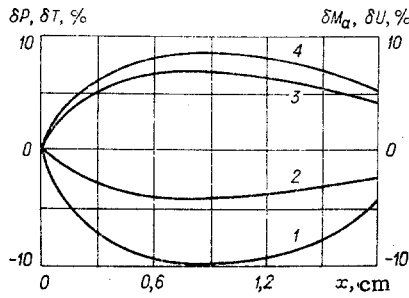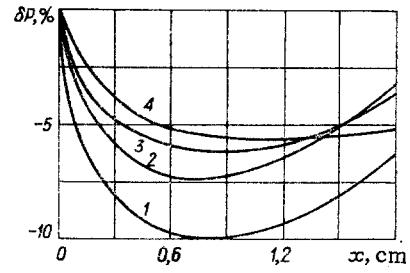
Fig. 1

Fig. 2

$$\delta T = \frac{T - T_0}{T_0} = \frac{1 - \varkappa M_a^2}{C_p T_0 \left(1 - M_a^2\right)} J',$$

$$\delta p = \frac{p - p_0}{p_0} = -\frac{\rho_0 \left(\varkappa - 1\right) M_a^2}{p_0 \left(1 - M_a^2\right)} J',$$

$$\delta \rho = \frac{\rho - \rho_0}{\rho_0} = -\frac{p_0 \left(\varkappa - 1\right) \varkappa}{\left(1 - M_a^2\right) \rho_0} J', \qquad (7)$$

$$\delta u = \frac{u - u_0}{u_0} = \frac{M_a^2 \left(\varkappa - 1\right)}{u_0^2 \left(1 - M_a^2\right)} J', \quad J' = \int\limits_0^x J \, dx.$$

Here T_0, p_0, ρ_0, u_0 are the macroscopic parameters of the unperturbed stream.

It is seen from (7) that the maximum values of δT, δp, $\delta \rho$, δu will be achieved for $M_a = 1 \pm \varepsilon$, where ε is a small quantity ($\varepsilon > 0$). As $M_a \to 0$

$\delta p \to 0$, $\delta u \to 0$, $\delta \rho \to \frac{p_0}{\rho_0} \varkappa (1 - \varkappa) |J'|$, $\delta T \to -\frac{|J'|}{C_p T_0}$, and as $M_a \to \infty \delta p \to \frac{p_0 (1 - \varkappa) |J'|}{p_0}$, $\delta T \to \frac{\varkappa |J'|}{C_p T_0}$, $\delta \rho \to$

0, $\delta u \to \frac{(\varkappa - 1) |J'|}{u_0^2}$, i.e., the temperature and velocity changes for a supersonic flow velocity

are greater than at a subsonic velocity $(0 < M_a < 1/\sqrt{\varkappa})$. On the other hand, the density changes strongly at a subsonic flow velocity. Let us note that for $M_a = 1/\sqrt{\varkappa}$ the gas translational temperature does not change despite the energy exchange between the translational and vibrational motions of the molecules in the mixture.

To illustrate the results obtained let us consider the flow of specific gases, e.g., N_2O and the mixture N_2O-N_2 in a field of radiation with frequency $\nu_{mn} = 917.4$ cm^{-1}, which is the resonance frequency of the transition P20[00°1 $\to$ 10°0] in the molecule N_2O. Numerical integration of the complete system of equations of gasdynamics and vibrational kinetics was carried out by using, as in [16], an implicit difference scheme of second-order accuracy. The relaxation scheme of the processes in the mixture N_2O-N_2 and its corresponding probability of elementary processes were taken the same as in [7].

The spectral magnification index was computed by means of standard relationships [8]. The magnitudes of the Einstein coefficient A_{mn} and of the shock broadening section σ_{N_2O-i} were taken, in conformity with [9], equal to : $A_{mn} = 0.278$ sec^{-1}, $\sigma_{N_2O-N_2O} = 7 \cdot 10^{-15}$ cm^2, $\sigma_{N_2O-N_2} = 7.7 \cdot 10^{-15}$ cm^2. Results of computing the change in macroscopic parameters in the absorption zone are represented in Fig. 1 for the flow of nitrogen oxide with the initial parameters $T_0 = 1000°K$, $p_0 = 0.002$ MPa, $M_0 = 1.02$ in a radiation field with $I = 2$ kW/cm^2. Curves 1-4 exhibit the change in pressure, temperature, velocity and Mach number governed by the "frozen" speed of sound. From the distributions represented it is seen that the maximal change during energy liberation (or energy absorption) is characteristic for the statistical pressure. Under the conditions considered $(\delta p)_{max} = 10\%$. Such a magnitude of δp can easily be recorded in experiment. Also seen clearly are domains with a different sign of the gradient of the macroscopic parameters in which cooling (V–T exchange) and heating (V–V' exchange) of the gas occur.
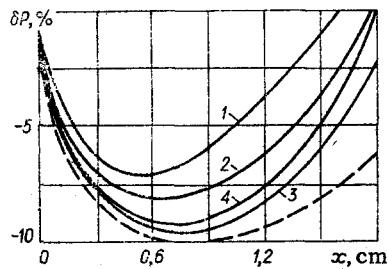
Fig. 3

The introduction of an impurity gas (in this case N_2) results in a substantial change in the profile of the macroscopic parameters in the absorption zone. The greatest change in the gradients of p, T, u and ρ is here characteristic for the heating domain where the energy flux in the translational degrees of freedom of motion of molecules from the upper level of the N_2O absorbing transition (00°1) diminishes because of the effective energy sink of the asymmetric vibrations in the "cold reservoir," which are the unperturbed molecules N_2. This is seen in Fig. 2, where the change in the quantity δp over the length of the absorption zone is shown for a flow of N_2O-N_2 mixtures with different N_2 content (curves 1-4 correspond to γ_{N_2} = 0; 0.2; 0.4 and 0.6).

To estimate the sensitivity of the method proposed for determining the relaxation time, nitrogen oxide flows were computed for different values of the velocities of the V–T and V–V' processes. The results of these computations are represented in Fig. 3 (the unperturbed stream parameters are the same as in the previous case). Here the numbers 1 and 2 correspond to curves of the pressure change obtained for a 1.5 and 2 times increase in the V–T relaxation velocity for the deformation mode of the N_2O molecule, respectively; and the numbers 3 and 4 also correspond to a 1.5 and 2 times increase in the intramolecular V–V' exchange velocity. The dashed curve displays the change in δp for normal velocities of the V–T and V–V' processes. It is seen that a 50% change in the V–T and V–V' exchange velocities will result in a substantial change also in the profiles of the macroscopic parameters (the pressure, say) in the absorption zone (the maximum difference in δp can here reach 7.5%).

Therefore, it follows from the results represented that the nature of the change in the macroscopic parameters of a moving gas in the resonance radiation absorption zone depends substantially on the magnitude of the V–T and V–V' process velocities, which permits determination of the characteristic times of the V–T and V–V' exchange processes in the absorption zone by means of the experimentally measured pressure, velocity, or temperature profile.

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