TRANSIENT PROCESSES IN VIBRATIONALLY EXCITED DIATOMIC GAS WITH DOWNWARDS FLUX OF QUANTA

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UDC 621.373.826.038.823

The kinetic cooling and formation of absolute inversion are studied numerically for the cases of a jump in the translational temperature of a vibrationally excited gas and instantaneous admixing of unexcited gas.

1. It is now well known [1] that the vibrational distribution of diatomic molecules under conditions of strong vibrational nonequilibrium can be very different from the Boltzmann distribution. In most physical situations the molecules are excited (in a discharge or optically) into low-lying levels, while owing to positive anharmonicity vibrational—vibrational (VV) exchange leads to occupation of high-lying levels and the formation of a "shelf" in the distribution function. In this process the number of vibrational quanta is conserved, but the vibrational quanta are "broken up," and this is accompanied by heating of the gas. The dynamics of these processes has been well studied; in particular, self-similar solutions describing the change in the shelf in time have been obtained [2]. This dynamics is characterized by a definite relation between the vibrational temperature of the lower-lying (first) levels T_1 and the level of the "shelf." In addition, T_1 is related with the temperature of the gas according to the law $T_1 \sim \sqrt{T}$ [3].

There arises the question: what does the evolution of the vibrational distribution function (VDF) look like, if the temperature of a strongly nonequilibrium gas increases in a jumplike fashion, for example, owing to a shock wave or sharp compression of the gas? If the source of excitation into the lower lying levels is switched off, then the increase in the temperature T_1 required for satisfying the condition $T_1 \sim \sqrt{T}$ should occur owing to pumping of vibrational excitation over from higher lying levels. VV exchange in this direction is accompanied by "enlargement" of the quanta and therefore should lead to cooling of the gas. In the process conditions for establishing on part of the VDF Trinor's law will exist (see [1]), i.e., the distribution with an absolute inversion corresponding to zero flux of vibrational quanta will arise. Indeed, the second of the indicated effects was observed in [4], where the passage of a shock wave through a vibrationally excited gas was modeled.

To observe these two effects – cooling of the gas in the process of VV exchange and formation of an absolute inversion – the value of T_1 must obviously be sharply reduced compared with the quasistationary value, determined in the case of pulsed pumping from the relation

$T_1=\frac{E_1}{4,6}\sqrt{\frac{T}{\Delta E}}$ [3]. This can be done by reducing the population of the lower lying vibrational levels, for example, by admixing unexcited gas or transferring particles into an electronically excited state (an almost resonant gas can be admixed, for example, CO can be admixed with N_2, CO_2, N_2O). The admissible rate of the effect under study is limited by VT relaxation on the upper levels and in the absence of such processes by VV exchange on the upper levels, in the course of which the gas is heated. It should be expected that the formation of an absolute inversion will be observed in a wider range of parameters and for a longer time than VV cooling.

To check foregoing assertions a series of calculations of the vibrational kinetics for the case of a jump in the gas-dynamic parameters, corresponding to a shock wave, and a jump in the composition corresponding to instantaneous admixing of undisturbed gas were performed.

Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 55, No. 4, pp. 624-629, October, 1988. Original article submitted May 19, 1987.

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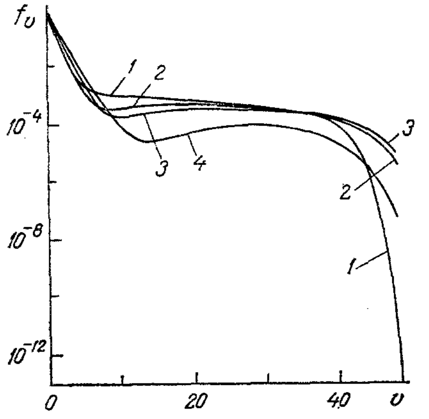

Fig. 1

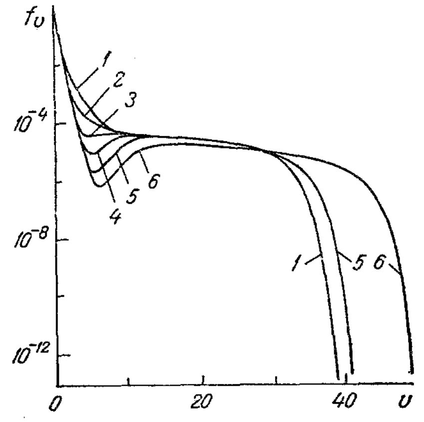

Fig. 2

Fig. 1. Evolution of the distribution function of CO molecules over the vibrational levels after the passage of a shock wave, M = 3.5 (T = 925 K): 1) t = 0.01; 2) 0.63; 3) 1.8; 4) 17 μsec.

Fig. 2. Evolution of the distribution function of CO molecules over vibrational levels accompanying mixing with unexcited CO (T = 204.3 K): 1) t = 0.01; 2) 0.13; 3) 0.4; 4) 1.2; 5) 7; 6) 49 μsec.

TABLE 1. Energy Balance in the Mixture CO:Ar after the Temperature Jump

t, sec	E_{CO}	W_{VV}	ΔE_{VV}	W_{VT}	ΔE_{VT}	T, K
5(—9)	1,49(—1)	—3,25(+3)	—1,8(—5)	6,4(+2)	3,5(—6)	925,53
2,2(—8)	1,49(—1)	—3(+3)	—6,9(—5)	6,4(+2)	1,4(—5)	925,50
7,3(—8)	1,49(—1)	—2,44(+3)	—2(—4)	6,6(+2)	4,7(—5)	925,42
2(—7)	1,49(—1)	—1,66(+3)	—4,6(—4)	6,9(+2)	1,4(—4)	925,28
6,3(—7)	1,49(—1)	—7,37(—2)	—9,2(—4)	8,4(+2)	4,7(—4)	925,18
1,8(—6)	1,49(—1)	—1(+2)	—1,3(—3)	9,7(+2)	1,6(—3)	925,79
5,5(—6)	1,46(—1)	—2,6(—1)	—1,35(—3)	6,3(+2)	4,5(—3)	928,04
1,7(—5)	1,42(—1)	—3,2(+1)	—1,81(—3)	1,7(+2)	8,43(—3)	930,76
5(—5)	1,4(—1)	—6	—2,33(—3)	3,7(+1)	1,09(—2)	932,29

Note. The plus and minus signs correspond to heating and cooling, respectively; 5(−9) denotes $5 \cdot 10^{-9}$.

2. In carrying out the calculations the complete system of equations of vibrational kinetics of diatomic anharmonic oscillators as employed (see, for example, [1]). The rate constants of the relaxational processes, the balance of the energy of the electrons, and the spectroscopic constants of the CO molecule were chosen in accordance with the results of [5]. The preliminary excitation of CO:Ar or N_2:Ar mixtures was modeled, and after some delay, necessary for forming the VDF, a perturbation corresponding to a shock wave or fast admixing of unexcited gas (accompanying flow through of the starting mixture) was superposed. The starting temperatures of the mixtures equalled 80 K, while the density equalled 0.5 amagat. The pump pulse had a duration of 100 μsec with an energy input of approximately 120 J/(liter·amagat). The changes in the parameters of the active medium behind the front of the shock wave were taken into account using the Hugoniot adiabat [6]:

$$P_2 = P_1\left(\frac{2\gamma}{\gamma+1}\,M^2 - \frac{\gamma-1}{\gamma+1}\right), \quad \rho_1 = \rho_2\left(\frac{\gamma-1}{\gamma+1} + \frac{2}{(\gamma+1)\,M^2}\right).$$

In addition, in performing calculations of variants with admixing of unexcited gas into a flow of excited gas it was assumed that the mixing is instantaneous and the translational temperatures of the excited and unexcited gases are equal.

3. The relaxational processes behind the front of the shock wave were calculated for different values of the Mach number of the incident wave, for different degrees of vibrational excitation of the molecules, and for different compositions of the mixtures (except that the

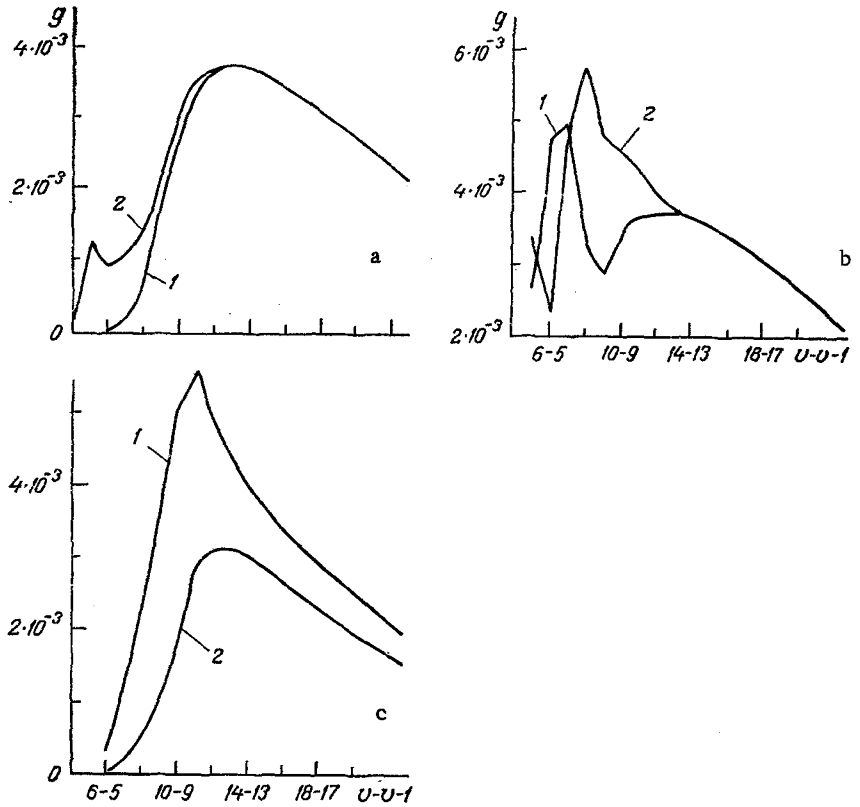

Fig. 3. Dynamics of the distributions of the maximum gains on vibrational transitions after admixing of unexcited CO: a) t = 0.01 (1) and 0.13 μsec (2); b) t = 0.4 (1) and 1.2 μsec (2); c) t = 7 (1) and 49 μsec (2). g is given in cm^{-1}.

mixtures CO:Ar and N_2:Ar were also pure CO). The typical evolution of the distribution function over the vibrational levels of the CO molecule after the passage of a shock wave in the mixture CO:Ar ≈ 1:10 is shown in Fig. 1.

The jumplike increase in the temperature of the vibrationally excited gas behind the front of the shock wave leads to a significant decrease in the gain on the vibrational–rotational transitions of the CO molecule. Thus, for example, under the conditions corresponding to Fig. 1, the maximum values of the gain on the transitions in the P branch immediately after the excitation are of the order of 10^{-3} cm^{-1}. As the absolute inversion forms, the gains on the lower vibrational levels ($v < 30$) do not increase, but rather decrease severalfold. This is associated with the decrease in the populations of the vibrational levels, occurring in the process of formation of an absolute inversion.

The computed magnitude of the kinetic cooling effect in the mixtures CO:Ar immediately after the jump in the temperature depends strongly on the degree of vibrational excitation of CO molecules and on the magnitude of the temperature jump. The largest kinetic cooling was obtained in calculations for values of the relative populations of vibrational levels in the region of the plateau of the distribution function, constituting ~10^{-3}, and for Mach numbers M ≈ 3-4 of the incident wave. The computational results for the mixture CO:Ar = 1:10 under conditions corresponding to Fig. 1, demonstrating the rate and magnitude of cooling in VV exchange processes, are presented in Table 1.

As one can see from Table 1, the highest cooling power, associated with VV exchange processes, is realized immediately after the perturbing action of the temperature jump, after which this effect, gradually weakening, continues approximately up to 50 μsec. The accompanying decrease in the translational temperature, however, is very brief and insignificant (~0.5 K) because of the competing effect of VT relaxation, which is appreciable at such short times even when an inefficient relaxant, such as argon, is employed as the diluent. Analogous calculations were performed for the mixture N_2:Ar approximately for the same values of the degree of vibrational excitation of the molecules and the magnitude of the temperature jump. Their results were very close to those obtained for the mixtures CO:Ar. The main difference lies in the fact that in the mixture N_2:Ar, owing to the lower rate of VV exchange between the N_2 molecules, VT relaxation plays a larger role and there is no cooling of the mixture. However, the maximum energy effect in the exchange processes proceeding with absorption of energy is close to that obtained in calculations for the mixture CO:Ar.

The computed population distributions over the vibrational levels of CO molecules with admixing of unexcited carbon monoxide to the excited mixture CO:Ar = 1:10, leading to the composition CO:Ar = 3:10, are presented in Fig. 2. As a result of the transfer, following the mixing process, of vibrational quanta to the lower levels, the populations on neighboring levels decrease systematically. After the excitation reaches the Trinor minimum, a characteristic "dip" is formed in the distribution function; an absolute inversion is present on the right side of the dip. At later stages of relaxation the population of the upper vibrational levels increase, and the level of the shelf in the distribution function drops somewhat. The corresponding dynamics of the distributions of the maximum gains over the vibrational transitions is shown in Fig. 3. One can see that after admixing of the unexcited gas appreciable amplification occurs primarily on comparatively low-lying transitions, on which amplification did not initially occur. The lowest transition with amplification was obtained at the time 0.4 μsec. Then the gain on these transitions decreases, and the maximum of the gain distribution gradually shifts toward higher vibrational transitions, so that amplification on them exceeds the initial level. The time during which the amplification on the transition 12 → 11 was preserved at a level close to the initial level equalled ~50 μsec.

These calculations also confirmed the existence of kinetic cooling of the mixture CO:Ar in VV exchange processes. Thus, for example, for the conditions of the dependences in Figs. 2 and 3 the maximum drop in the temperature equalled 0.3 K over 30 μsec, after which the sign of the total temperature effect of VV exchange processes changed and gradual heating started. VT relaxation at these times has virtually no influence on the magnitude of the effect; it starts to have an effect later.

In addition to the case with a threefold increase in the concentration of CO molecules as a result of admixing, the calculations were also performed with a doubling of the concentration of CO molecules. In this case the cooling and increase in the amplification were weaker, and the width of the maximum in the dependence of the gain on the number of the vibrational level is appreciably smaller.

Thus, the calculations performed confirmed the validity of the arguments given at the beginning of this paper. It was shown that the kinetic cooling effect owing to VV exchange is small and its magnitude is sensitive to the ratio of VV and VT processes as well as to the competition between the contributions from the upper and lower levels. The formation of an absolute inversion is more stable, it can be easily observed, and it is especially large when excited and unexcited gases are mixed. One can hope that this effect can be used to extend the spectral range of lasing of CO lasers.

NOTATION

T_1, vibrational temperature of the first vibrational level of the CO molecule; E_1, energy of this level; T, translational temperature of the gas; ΔE, anharmonicity of the CO molecule; M, Mach number: P_2, ρ_2, P_1, and ρ_1, pressure and density of the gas behind the front of the shock wave and in front of the shock wave; γ, adiabatic index; E_{CO}, ΔE_{VV}, ΔE_{VT}, vibrational energy stored in the CO molecules and the total energy effects of the VV-exchange and VT-relaxation processes [J/cm³]; W_{VV} and W_{VT}, total rates at which energy is released in VV exchange and VT relaxation processes [W/cm³].

LITERATURE CITED

1. B. F. Gordiets, A. I. Osipov, and L. A. Shelepin, Kinetic Processes in Lasers and Molecular Lasers [in Russian], Moscow (1980).
2. S. A. Zhdanok, A. P. Napartovich, and A. N. Starostin, Zh. Éksp. Teor. Fiz., 76, No. 1, 130-139 (1979).
3. A. V. Dem'yanov et al., Zh. Prikl. Mekh. Tekh. Fiz., No. 3, 5-10 (1981).
4. S. A. Losev and V. N. Makarov, Kvantovaya Élektron., 12, No. 8, 1628-1631 (1985).
5. A. A. Ionin et al., "Investigation of the lasing characteristics of an electroionization CO laser based on nitrogen-containing mixtures," Preprint No. 232, Quantum Radiophysics, Physics Institute of the Academy of Sciences of the USSR, Moscow (1982).
6. L. D. Landau and E. M. Lifshits, Hydrodynamics [in Russian], Moscow (1986).