

NONEQUILIBRIUM VIBRATIONAL EXCITATION OF MOLECULES
BEHIND A SHOCK WAVE FRONT IN GASEOUS MIXTURES

S. V. Dobkin and É. E. Son

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The process of vibrational excitation of molecules behind shock waves usually proceeds as follows [1]: at a distance of the order of several molecular mean free path lengths, the kinetic energy of translational motion of molecules is transformed into the energy of random motion, which increases the gas temperature behind the shock wave front. Then, energy is exchanged between the vibrational and translational molecular degrees of freedom. Due to the rapid V-V exchange, a Boltzmann distribution of molecules over vibrational levels is established with temperature T_V , which in the process of vibrational excitation increases monotonically from a value equal to the temperature of the gas entering into the front of the shock wave T_0 to the value of the translational temperature T_1 behind the shock wave front. We will refer to the process of vibrational excitation behind the shock wave front described above as an equilibrium process.

It was shown in [2] that when a shock wave propagates in a light-weight gas with a small admixture of a heavy gas the translational relaxation length of heavy molecules is approximately a factor of m_G/m_L greater than for the light-weight molecules (m_G and m_L are the masses of the heavy and light components). This effect is related to the fact that the fraction of the energy transferred in a collision between a heavy particle and a light particle is small, and for this reason a large number of collisions is necessary to stop the heavy particle.

We will analyze qualitatively the phenomena occurring as molecules consisting of atoms with masses m_H and m_F are stopped in a medium consisting of particles with mass m_L ($m_H \gg m_F \gtrsim m_L$). This case is related, for example, to propagation of a shock wave in helium or argon with a small admixture of UF_6 molecules.

The velocity of the gas before and after the shock wave front and the temperature of the monatomic gas are related by the relations

$$\frac{U_1}{U_0} = \frac{M_0^2 + 3}{4M_0^2}, \quad \frac{T_1}{T_0} = \frac{5}{16} M_0^2 \left(1 - \frac{1}{5M_0^2} \right) \left(1 + \frac{3}{M_0^2} \right),$$

where $M_0 = U_0/a_0$; a_0 is the velocity of sound in the gas in front of the shock wave front. The size of the zone of translational relaxation of light-weight particles (the width of the shock wave) is $l_L \sim (n_L \sigma_{LL})^{-1}$ and that of heavy molecules is $l_G \sim (m_G/m_L) l_L$ (n_L is the concentration of light-weight particles behind the front, σ_{LL} is the cross section for elastic scattering) and, for this reason, behind the shock wave front there exists a large region where heavy molecules have kinetic energy of directed motion which, on collisions with atoms, can lead to vibrational excitation of molecules consisting of F and H atoms or H and H. If the parameters of the atomic interaction potentials F-L and H-L are identical, then vibrational excitation of the FH molecule will occur most efficiently, since, on the one hand, such a molecule has the longer stopping distance compared to FF and, on the other, it has the highest probability for exciting vibrations compared to HH. The directed velocity of heavy particles in front of the shock wave front exceeds the random velocity of light-weight particles behind the shock wave front and, for this reason, a situation can occur in which the vibrational temperature of the admixture molecules exceeds the gas temperature behind the shock wave front, so that subsequent vibrational relaxation occurs in a nonequilibrium manner (Fig. 1a, curve 2) with excitation involving energy exchange, opposite to that of the "equilibrium" excitation (Fig. 1a, curve 1) (l_L , l_G , and l_{VT} are the translational relaxation lengths of light-weight and heavy molecules and the vibrational relaxation length of the molecules; in Fig. 1b, curve 1 is for light-weight particles and curve 2 is for heavy particles).

Let us calculate the fraction of vibrational energy transferred to a molecule as it is slowed down in a light-weight gas. In so doing, we will neglect the narrow zone of translational relaxation of light-weight particles. It is well known [3] that when a shock wave propagates in a binary mixture, as a result of diffusion, the light-weight component concentrates on the shock wave front. The width of the zone in which particles concentrate $\Delta x \sim D/U_0$ (D is the diffusion coefficient) is of the order of a mean free path length of light-weight

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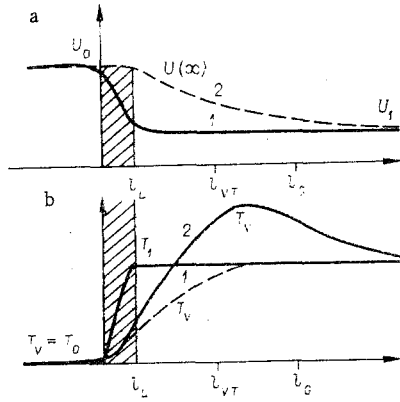


Fig. 1

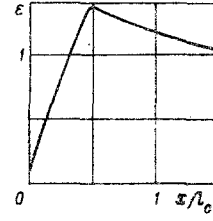


Fig. 2

particles or the width of the translational relaxation zone of the light-weight component, which we neglect.

Let us examine relaxation of vibrational energy of molecules described by harmonic oscillators in the zone where they are stopped in the light-weight gas behind the shock wave front. The kinetic equations for the population density of the i -th vibrational state in the single-quantum approximation for V-V exchange have the form

$$\begin{aligned} \frac{\partial N_i}{\partial t} + U \frac{\partial N_i}{\partial x} = \nu (N_{i-1} P_{i-1,i} - N_i P_{i,i-1} + N_{i+1} P_{i+1,i} - N_i P_{i,i-1}) + \sum_{i'} (N_{i-1} N_{i'+1} Q_{i-1,i}^{i'+1,i'} - N_i N_{i'} Q_{i,i-1}^{i',i'+1} + N_{i+1} N_{i'-1} Q_{i+1,i}^{i'-1,i'} - N_i N_{i'} Q_{i,i+1}^{i',i'+1}), \end{aligned} \quad (1)$$

ν is the frequency of collisions leading to V-T exchange. Terms containing P and Q describe, respectively, V-T and V-V exchange. The equation for vibrational energy per unit volume

$$E = \hbar\omega \sum N_i i / N \quad (2)$$

does not contain terms with V-V exchange which do not change E. Taking into account, in addition, that for harmonic oscillators $P_{i+1,i} = (i+1)P_{10}$, $P_{i,i+1} = (i+1)P_{01}$, we obtain a well-known equation for relaxation of vibrational energy. For stationary motion of the gas, it has the form

$$U \frac{dE}{dx} = -\nu_L C P_{10} (1-z)(E - E^{(0)}); \quad (3)$$

$$E^{(0)} = \hbar\omega z / (1-z), \quad z = P_{01} / P_{10}. \quad (4)$$

In the state of thermodynamic equilibrium, $z = z_p = \exp(-\hbar\omega / T)$. In nonequilibrium vibrational excitation and relaxation that we are examining, heavy molecules are stopped in the light-weight gas over a greater distance compared to the mean free path length of light-weight molecules and, for this reason, the rate of vibrational excitation and relaxation will depend on the magnitude of the directed velocity of the molecules. Or, in other words, in order to determine the average probabilities P_{01} and P_{10} , it is necessary to average the transition probabilities over the Maxwell distribution function, shifted by the magnitude of the relative velocity of light-weight and heavy molecules $\Delta U(x) = U(x) - U_1$:

$$f_L(x, \mathbf{v}) = \left(\frac{m_L}{2\pi T_1} \right)^{3/2} \exp \left\{ -\frac{m_L [\mathbf{v} - \Delta U(x)]^2}{2T_1} \right\}. \quad (5)$$

Here, it is assumed that the distance over which a Maxwell distribution is established (of the order of the mean free path length of light-weight molecules) is less than the distance over which $U(x)$ changes appreciably, i.e., $l_L dU/dx \ll \Delta U$.

We will take the probability for excitation and deexcitation of vibrations in the adiabatic approximation, taking into account the principle of detailed balance. According to [4], the adiabatic probabilities $P_{10}(v)$, $P_{01}(v)$ for an exponential potential describing repulsion of light-weight gas atoms from molecules, taking into account the principle of detailed balance, must be written in the form

$$P_{01}(v) = A \exp \left[-\frac{2\pi a \omega}{v} \left(1 + \frac{\hbar\omega}{2\mu v^2} \right) \right]; \quad (6)$$

$$P_{10}(v) = A \exp \left[-\frac{2\pi a \omega}{v} \left(1 - \frac{\hbar \omega}{2\mu v^2} \right) \right], \quad (7)$$

where $\mu = m_G m_L / (m_G + m_L)$; A is the pre-exponential multiplier, which we assume does not depend on the velocity of the particles. We will carry out the calculations in the adiabatic approximation, assuming that the adiabaticity parameter is large ($\xi = \pi a \omega (m_L / 2T_1)^{1/2} \gg 1$). In this case, the term $\hbar \omega / 2\mu v_0^2 \sim (\hbar \omega / T_1) \xi^{-2/3} \ll 1$ in (6) and (7), so that it can be assumed to be small correction and in integrating over the distribution (5) its value at the point of the maximum in the integrand can be taken out from under the integral sign. Calculation of the average probabilities using the saddle point method leads to the following expressions:

$$\bar{P}_{01}(u) = \int P_{01}(v) f_L(x, v) d^3v = P_{01}(T_1) \exp \left[-\frac{\hbar \omega}{2T_1} \right] \text{ch} [u\alpha(1 + \beta)]; \quad (8)$$

$$\bar{P}_{10}(u) = \int P_{10}(v) f_L(x, v) d^3v = P_{01}(T_1) \exp \left[\frac{\hbar \omega}{2T_1} \right] \text{ch} [u\alpha(1 - \beta)], \quad (9)$$

where $u(x) = [U(x) - U_1] (m_L / 2T_1)^{1/2}$, while the dimensionless parameters $\alpha = 2\xi^{1/3}$ and $\beta = \hbar \omega / 6T_1 \xi^{2/3}$.

The collision frequency ν_{LG} , entering into Eq. (3), also must be averaged over the velocity distribution function (5). If the elastic scattering cross section σ_{LG} does not depend on velocity, then as a result of averaging, we obtain

$$\nu_{GL}(u) = (2T_1/m_L)^{1/2} n_L \sigma_{LG} [1 - \sqrt{\pi} u \Phi(u)], \quad (10)$$

$$\Phi(u) = (2\pi)^{-1/2} \int_0^u e^{-t^2/2} dt.$$

Equation (3) has a simple physical meaning. If at each point behind the shock wave front the distribution function over the vibrational degrees of freedom were established over a distance much less than the stopping distance of heavy molecules, then a quasistationary distribution would be established over vibrations with $E^{(0)}$ (4), where

$$z(u) = \frac{P_{01}(u)}{P_{10}(u)} = e^{-\hbar \omega / T_1} \frac{\text{ch} [u\alpha(1 + \beta)]}{\text{ch} [u\alpha(1 - \beta)]}. \quad (11)$$

Due to the rapid V-V exchange, the distribution function must be a Boltzmann function with vibrational temperature $T_V(x)$, defined by the relation

$$\frac{T_V(x) - T_1}{T_1} = \frac{2u(x)}{3\xi^{1/3}}, \quad (12)$$

which is obtained from (11) by expanding with respect to the small parameter α^{-1} . But, in reality, vibrational excitation occurs at a finite rate [time $\tau_{VT} \sim (\nu_{LG} P_{10})^{-1}$] and Eq. (3) describes relaxation of vibrational energy to $E^{(0)}(u)$.

Substituting into (12) the value of the velocity U_0 on the wave front, it is possible to obtain a useful upper estimate for the largest possible excess of the vibrational temperature above the equilibrium value.

In what follows, for the velocity distribution behind the shock wave front, we will use the approximate equation for stopping heavy particles in a medium consisting of light-weight particles [2]

$$U \frac{dU}{dx} = -\beta_G (U - U_1), \quad \beta_G = \frac{m_L}{m_G} U_1 n_L \sigma_{LG} C^{-1}, \quad (13)$$

$$C = \left[\frac{128(5M_0^2 - 1)}{15\pi(M_0^2 + 3)} \right]^{1/2}.$$

Equation (13) is valid if the relative velocity of heavy and light-weight particles is small compared to the average thermal velocity of the light-weight particles [i.e., in the region where $\Delta U(x) \ll 1$]. In a more rigorous formulation, it is necessary to take into account the exact dependence of the drag force on the relative velocity [5].

Equation (3) must be supplemented by a boundary condition. In this paper, we will choose this condition as follows: an equilibrium distribution over vibrational degrees of freedom exists on the shock wave front with temperature $T_V = T_0$. Normalizing the vibrational energy to its equilibrium value on the shock wave front ($T_V = T_1$) and substituting (4)-(13) into (3), we obtain the equation

$$\frac{d\varepsilon}{du} = \frac{-\varepsilon^{(0)}(u) + \varepsilon}{\tau(u)}, \quad \varepsilon(u_0) = \frac{E_p(T_0)}{E_p(T_1)},$$

$$\tau(u) = \frac{\beta_G}{v_{LG}} \frac{u}{P_{10}(u)[1-z(u)]}, \quad u_0 = [U_0 - U_1](m_L/2T_1)^{1/2}. \quad (14)$$

The variable u is related to the distance x from the shock wave front by the relation

$$x/l_G = \sqrt{2}C[A(u_0 - u) + \ln(u_0/u)], \quad A = (2T_1/m_L)^{1/2}/U_1,$$

following from (13).

We will analyze qualitatively the solution of Eq. (14): usually, the temperature behind the shock wave front is higher than the initial temperature. For this reason, for $u(x) \leq u_0$, $\varepsilon^{(0)}(u) \gg \varepsilon(u_0)$ and it is possible to neglect the term ε on the right side of Eq. (14). Taking into account the fact that in this region the parameter $\alpha \gg 1$ and carrying out the corresponding expansion with respect to this parameter, we obtain

$$\varepsilon(u) = \varepsilon(u_0) + B[E_i^*(\gamma u_0) - E_i^*(\gamma u)],$$

$$E_i^*(x) = \int_{-\infty}^x \exp(t)/t dt, \quad (15)$$

$$\gamma = \alpha + 2\beta, \quad B = \frac{m_G}{m_L} AC \frac{P_{10}(T_1)}{2} [1 - \exp(-\hbar\omega/T_1)].$$

For $u \rightarrow 0$, $\varepsilon(u) \rightarrow \varepsilon^{(0)}(u)$. The solution can be joined, for example, at the point u^* defined by the equation

$$\varepsilon(u^*) = \varepsilon^{(0)}(u^*).$$

We note that in the case that the condition of adiabaticity is not satisfied, as often occurs with collisions, for example, between particles that have very different masses [4], the theory of nonequilibrium vibrational excitation developed does not lose its meaning. In this case, only the transition amplitudes change in (6) and (7), and in subsequent calculations it is not necessary to carry out an expansion, while it is necessary to use more complicated expressions similar to (8)–(14). But, apparently, the conclusion that the vibrational temperature exceeds the equilibrium value remains valid and the estimates presented above will turn out to be useful.

Let us analyze the characteristic magnitudes of the parameters using as an example the propagation of a shock wave in helium with a small admixture of UF_6 . According to [6, 7], the multimode UF_6 molecule is described with good accuracy by a two mode approximation, in which the lower modes are combined into a single mode with an energy quantum $\hbar\omega_1/k = 253^\circ\text{K}$ and the upper modes are combined into a single mode with an energy quantum $\hbar\omega_2/k = 876^\circ\text{K}$. The frequency for exchange of vibrational quanta between modes is $K_2 = 4.5 \cdot 10^5 \text{ p}(\text{Pa}^{-1} \cdot \text{sec}^{-1})$, and the V–T relaxation rate of the lower mode in collisions with argon atoms is $p\tau_{VT} = 6 \cdot 10^{-4} \text{ Pa} \cdot \text{sec}$ and with UF_6 molecules $p\tau_{VT} = 4.4 \cdot 10^{-4} \text{ Pa} \cdot \text{sec}$. In a mixture with He, these parameters, apparently, do not change significantly. For this reason, we will examine the example of a shock wave in helium with a small admixture of UF_6 , since because of the appreciable ratio of the masses in this mixture, the effects being examined could possibly be observed in this mixture. We will choose the parameters of the mixture in front of the shock wave front as follows: $M_0 = 5$, $T_0 = 300^\circ\text{K}$, $p_0 = 1 \text{ kPa}$. Then the width of the transitional relaxation zone for the light-weight component is $l_L \approx 5 \cdot 10^{-3} \text{ cm}$ and the characteristic stopping time for the heavy particle is $\tau_G \approx l_G/U_0 \approx 0.9 \cdot 10^{-6} \text{ sec}$. This time greatly exceeds the period of the molecular vibrations, $\omega^{-1} \ll \tau_G$. The V–T relaxation time ($\tau_{VT} \approx 0.2 \cdot 10^{-7} \text{ sec}$) is less than the retardation time of a heavy molecule and greater than the V–V exchange time ($\tau_{VV} < K_2^{-1} \approx 0.2 \cdot 10^{-8} \text{ sec}$) $\tau_{VV} \ll \tau_{VT} \ll \tau_G$. Thus, the characteristic times correspond to the model being examined.

We will limit ourselves to examining pumping only of the lower mode of the UF_6 molecule, through which V–T exchange will occur most intensively, since the V–V exchange time between modes is much less than the characteristic V–T relaxation time. Although in deriving (14) the Landau–Teller approximation was used, taking into account the V–T relaxation rate of a polyatomic molecule, which can turn out to be greater than that examined in the present model [4], will only increase the vibrational temperature of the molecule. The calculation is only illustrative due to the absence of data on the temperature dependence of the vibrational excitation probabilities of the UF_6 molecule. Figure 2 shows the dependence of the vibrational energy of the lower mode of UF_6 on the distance x to the shock wave front (mixture of He and UF_6). Here, we use the following values of the parameters: $\xi = 8$, $P_{10}(T_1) = 0.04$.

The effect examined can, apparently, be observed experimentally by following the concentration of the first vibrationally excited state. The characteristic width of the relaxation zone of the vibrational temperature is $\Delta x \sim l_G \approx 0.4 \text{ cm}$.

In stronger shock waves, the effect can lead, in particular, to the existence of a zone with a high degree of dissociation of molecules, while the latter attains an equilibrium value behind the region in which the heavy molecules are stopped, if there are no admixtures that actively couple the reaction products.

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PROBLEM OF OBTAINING A POPULATION INVERSION IN VIBRATIONAL LEVELS OF POLYATOMIC DIPOLE MOLECULES BEHIND A SHOCK-WAVE FRONT

V. A. Levin and A. M. Starik

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The possibility for an inversion to arise with the breakdown of thermodynamic equilibrium as a result of a sharp increase in the temperature of a mixture of polyatomic molecules, having different relaxation times for free vibrations, was first examined in [1]. However, in spite of the fact that in [2] lasing was detected behind the front of an overdriven detonation wave in a F_2O-H_2-Ar mixture, in practice this method has not been widely used. This is related, apparently, to the fact that the calculations of the flow of CO_2-N_2-He (H_2O) mixtures behind the front of a strong shock wave carried out in [3, 4] indicated a very small size for the region in which the inversion exists of about 0.2 cm [4]. And, although the value of the inverted population density for the transitions $04^0 \rightarrow 00^01$ and $20^0 \rightarrow 00^01$ in the CO_2 molecule was comparable to the inverted population density of molecules with expansion in supersonic nozzles $\sim 10^{14}-10^{15} \text{ cm}^{-3}$, it is very difficult to observe it and to generate laser radiation with very small gains ($\sim 0.005 \text{ m}^{-1}$) in such thin layers.

The difficulties of choosing an active medium for a laser, using the method of fast heating for disrupting thermodynamic equilibrium, are related to the necessity of providing for high pumping rates to the upper laser level. Since initially the translational temperature behind the front of a shock wave is high, while the population density of vibrational levels corresponds to the equilibrium temperature in front of the shock wave front [5], the rate of excitation of molecules in this case is determined by the rate of the V-T process for modes having the shortest relaxation time. For this reason, one of the requirements for molecules in the active medium in obtaining an inversion by the rapid heating of the mixture is a high rate for V-T processes. This is also indicated by the results of [6], wherein the possibility of the formation of an inversion behind a shock wave front as the wave passes through a mixture containing (CO_2 , N_2O) molecules with different V-T relaxation times, τ_j , was analyzed.

The smallest values of τ_j , with other conditions being equal, are characteristic for unsymmetrical dipole molecules. For example, the rate of excitation of the deformation vibrations in the V-T process for H_2O molecules is 50 times greater than the corresponding value for CO_2 even in a mixture with He. The use of such molecules will also provide acceptable gains (due to the high Einstein coefficients) even with low inverted population densities of the particles. The possibility of obtaining an inverted population with rapid heating of a gas consisting of dipole molecules in shock waves was first examined in [7] for H_2O molecules.

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