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Abstract

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PHYSICS

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ON THE INFLUENCE OF ANHARMONICITY ON THE RELAXATION TIME UNDER ADIABATIC EXCITATION AND DEACTIVATION OF MOLECULAR VIBRATIONS

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In an experimental study of the process of vibrational excitation behind the front of a shock wave in oxygen and nitrogen, it was found that the value of the relaxation time τ of the mean vibrational energy ε of the gas, determined according to the equation

$$d\varepsilon/dt = (\bar{\varepsilon} - \varepsilon)/\tau, \tag{1}$$

($\bar{\varepsilon}$ is the value of ε in the state of equilibrium) is not constant in the zone of vibrational excitation. The increase in τ behind the shock-wave front in undiluted oxygen noted in (^{1}) is associated with a decrease in the temperature of the gas; in addition, however, a noticeable decrease in the value of τ is observed toward the end of the relaxation process ($^{2-4}$). In order to clarify this

[Fig. 1 and Fig. 2]

Fig. 1. Examples of the change in the vibrational relaxation time τ behind the shock-wave front in a mixture of 10% O_2 + 90% Ar at $T = 6000^\circ$ K (a) and in undiluted nitrogen when the temperature changes from 6500 to 6000°K (b). The thin vertical lines indicate the range of experimental values. The solid lines are the calculated change in τ according to relation (5). The value of τ is reduced to the normal gas density (the scale along the ordinate for variant (a) is enlarged by a factor of 5). t_l is the time in the laboratory frame of reference.

Fig. 2. Ratio of the current value of the vibrational relaxation time of molecular oxygen to the value τ^0 for a harmonic oscillator as a function of the vibrational temperature T_k. The numbers near the curves are the gas temperature in thousands of degrees. The arrows indicate the direction of motion of the relaxing system during isothermal excitation of vibrations (downward) and deactivation (upward). The dotted line is the limiting value of τ at $T_k = T$.

question, a more detailed investigation was carried out of the change in τ during vibrational relaxation in a mixture of 10% O_2 + 90% Ar (under conditions close to isothermal) and in undiluted nitrogen. The experiments were carried out on a shock···

tube by the method of absorption ultraviolet spectroscopy, described in detail earlier (^{4,5}).

Under nearly isothermal conditions, the value of τ behind the shock-wave front decreases continuously (Fig. 1a); in the case of an undiluted molecular gas, despite the drop in temperature, the value of τ, some time after passage of the shock-wave front, also begins to decrease (Fig. 1b) *. Thus, the relaxation time τ ceases to be a single-valued function of the gas temperature, which considerably complicates the interpretation of the experiment and the comparison of the results of different authors with one another and with theoretical calculations. In essence this means that equation (1) describes the process of vibrational relaxation insufficiently accurately, since it is strictly valid only for a model of molecules in the form of harmonic oscillators. Unfortunately, the attempts known in the literature to solve the problem of vibrational relaxation in a system of anharmonic oscillators have not yet led to a satisfactory replacement of (1) by a more accurate and not too complicated equation, which is connected with the difficulties of an analytical solution of such a problem. In a number of cases it is sufficient to know the relaxation time only to order of magnitude, which removes the need to refine (1). Nevertheless, in many problems a more accurate quantitative description of the process of vibrational relaxation in a real gas is necessary. One possible way of solving this problem is to use the assumption that, in the first approximation, equation (1) is also valid in a system of anharmonic oscillators; then corrections for anharmonicity should be sought for the value τ analogously to the way this is done for transport coefficients in the kinetic theory of gases for the hard-sphere model with corrections for the influence of the internal degrees of freedom of the molecules.

Such a correction is obtained most simply by considering only one-quantum transitions in the oscillator system, for which the probabilities $P_{k,k+1}$ of transitions between levels k, $k+1$ take anharmonicity into account in the form (^{6})

$$P_{k,k+1} = P_{01}(k+1)\gamma^k \equiv P_{01}(k+1)e^{4k\chi\varepsilon}, \tag{2}$$

where χ is the well-known parameter of the adiabatic theory of vibrational relaxation ($\chi = [2\pi^4 \mu k \theta^2 / a^2 h^2 T]^{1/3}$, for notation see § 2 (^{7})), ε is the anharmonicity parameter ($\varepsilon = \theta/4D$, θ is the characteristic vibrational temperature, D is the dissociation energy in degrees). Multiplying both sides of the balance equation for the population x_k of molecules on the k-th vibrational level by k

$$\left(\sum x_k = 1\right);$$

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Fig. 3

Figure 1: Fig. 3

$$dx_k/dt = P_{k+1,k}x_{k+1} - P_{k,k-1}x_k - P_{k,k+1}x_k + P_{k-1,k}x_{k-1} \tag{3}$$

and summing over k, after simple transformations with allowance for (2) and for the principle of detailed balance we arrive at a relation for τ/τ_0 (τ_0 is the value of τ for a system of harmonic oscillators) in the form

$$\tau/\tau_0 = \left[1 - \left(e^{\theta/T} - 1\right)\sum kx_k\right] / \left[\sum \gamma^k x_k - \left(\gamma^{-1}e^{\theta/T} - 1\right)\sum k\gamma^k x_k\right]. \tag{4}$$

In the case when, in the process of vibrational relaxation, the Boltzmann distribution of molecules over levels with the current value of the vibrational temperature T_k is preserved, it follows from (4) that **

$$\tau/\tau_0 = \left[(1 - \gamma\exp(-\theta/T_k))/(1 - \exp(-\theta/T_k))\right]^2. \tag{5}$$

This case corresponds best to the course of the process of vibrational excitation in a gas behind the front of a shock wave that is not too strong. According to (5), immediately behind the shock-wave front ($T_k \sim 0$), τ is close to τ_0; with the development of the process of vibrational relaxation, the ratio τ/τ^0 decreases, which is also observed in experiments (Fig. 1). The role of anharmonicity is thus reduced to an acceleration of vibrational excitation. Relation (5) is in good agreement with the results of an exact solution of a system of kinetic balance equations of type (3), since the Boltzmann distribution in the process of excitation of vibrations of anharmonic oscillators is violated only at the upper levels, whose contribution to the total vibrational energy is negligibly small because of their insignificant population (^{8}).

Relation (5) will describe the change in τ also during slow deactivation of vibrations (with preservation of the Boltzmann distribution at the lower levels). In this case, in the relaxation process the quantity τ will increase, remaining less than τ_0 (Fig. 2)*. The limiting value τ_∞ at complete statistical equilibrium (dashed line in Fig. 2, $T_k = T$) for an anharmonic oscillator is always less than τ_0.

Fig. 3. Ratio τ/τ_0 for molecular nitrogen with a substantial deviation from the Boltzmann distribution over levels; m is the level number. Solid lines are for a

* The gas pressure in this case changes insignificantly in all cases.

** Relation (5) is meaningful for $T_k \leq \theta/\ln\gamma$ and in the absence of multiquantum transitions.

δ-shaped distribution at the m-th level; dashed lines are for a "table-shaped" distribution with boundary at the m-th level. The numbers near the curves are the gas temperatures in thousands of degrees.

With rapid cooling of a gas in the process of deactivation of vibrations, significant violations of the Boltzmann distribution of molecules over the lower vibrational levels and even population inversion are possible. If, in this case, the so-called "table-shaped" distribution is realized ($x_0 = x_1 = \ldots = x_m,\ x_k = 0$ for $k > m$), then from (4) it follows that at this moment

$$\frac{\tau}{\tau_0} = \frac{(m+1)\left[\frac{1}{2}m\left(e^{\theta/T}-1\right)-1\right]}{\left(e^{\theta/T}-\gamma\right)\left(\dfrac{m\gamma^m}{\gamma-1}-\dfrac{\gamma^m-1}{(\gamma-1)^2}-\dfrac{\gamma^{m+1}-1}{\gamma-1}\right)}. \tag{6}$$

The corresponding values of τ/τ_0 for nitrogen are shown in Fig. 3 by dashed lines. Finally, in the limiting case of a δ-shaped distribution, in which all molecules are at the m-th level, this ratio is equal to

$$\frac{\tau}{\tau_0} = \frac{1}{\gamma^{m-1}}\frac{m\left(e^{\theta/T}-1\right)-1}{m\left(e^{\theta/T}-\gamma\right)-\gamma} \tag{7}$$

(solid lines in Fig. 3). From Figs. 2 and 3 it is seen that allowance for anharmonicity can lead to a substantial reduction in the time of vibrational deactivation compared with the values measured in shock waves, which is also noted in experiments on the measurement of τ during cooling of gas in nozzles (for example, ([9], [10])). Therefore, in a quantitative comparison of the results of experiments on the study of deactivation, it is also necessary to take into account the influence of anharmonicity.

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[*] Under real conditions, deactivation cannot proceed isothermally (temperature jumps are not realized in nature), and therefore the trajectory of the relaxing system on the graph in Fig. 2 will be more complicated.

Relation (5) makes it possible to find τ_0 for the dependences of τ on T_k and T obtained in shock-tube experiments. The values of τ_0 for nitrogen and for the mixture 10% O_2 + 90% Ar are presented in Fig. 4 in Landau-Teller coordinates. The value τ^0 exceeds previously published data by tens of percent at $T \approx \theta$ and by more than a factor of two at higher temperatures; thus, the refinement made in the value of the vibrational relaxation time affects the dependence of this quantity on temperature. The temperature interval shown in Fig. 4 is still not broad enough to permit comparison with the results of theoretical calculations.

Fig. 4. Dependence of τ^0 (at normal gas density) on temperature in Landau-Teller coordinates for the mixture 10% O_2+90% Ar (points) and nitrogen (lines).

Fig. 4. Dependence of τ^0 (at normal gas density) on temperature in Landau-Teller coordinates for the mixture 10% O_2 + 90% Ar (points) and nitrogen (lines)

Figure 2: Fig. 4. Dependence of τ^0 (at normal gas density) on temperature in Landau-Teller coordinates for the mixture 10% O_2 + 90% Ar (points) and nitrogen (lines)

Naturally, relation (5) refines the value of τ only in the first approximation. In experiments, especially at high temperatures, the value of τ toward the end of the relaxation zone changes somewhat more steeply than follows from (5) with γ determined according to (2). The agreement is improved with some increase of the parameter γ relative to the values recommended in [6]. On the other hand, under these conditions the influence of multiquantum transitions and of incipient molecular dissociation is possible.

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