ACCOMMODATION OF MOLECULAR VIBRATIONAL ENERGY USING
THE EFFECT OF A PRESSURE INCREASE IN A RAREFIED GAS ABSORBING
LASER RADIATION

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1. Introduction

Vibrational relaxation of gas molecules interacting with a solid surface has been investigated in a number of papers [1-4], in which various experimental methods of determining the coefficient of accommodation of vibrational energy on surfaces (ε) have been proposed and values of ε have been found for a number of molecules.

Knowledge of the values of ε is necessary in an investigation of the effects of laser stimulation of heterogeneous physicochemical processes, in the development and creation of low-pressure lasers, and in aerodynamic and gasdynamic research. In a number of problems (e.g., IR photochemistry) such information is required for polyatomic molecules, particularly molecules absorbing the radiation of a CO_2 laser. At present there are data on the values of ε only for certain complex molecules (CH_4, CF_3Cl, C_2H_4). They are presented most fully in [1]. The coefficients of accommodation of vibrational energy for such molecules are determined by methods based on measurement of the thermal conductivity of the gas [3], as well as of the pressure in a gas absorbing the IR radiation of a thermal source [4]. The values of ε obtained may be inaccurate, however. This is connected with the fact that the models used in these methods to describe the processes under study are insufficiently well founded and require refinement. In [4], in particular, in describing the effect of a pressure change Δp due to V—T relaxation of energy, only processes of vibrational excitation of molecules in the gas and of deactivation of their energy in the volume and on the cuvette wall were taken into account. The influence of the diffusion process on the value of ε was ignored. Estimating relations were used in the calculations, resulting in systematic errors in the determination of ε. The procedure of Δp measurements developed in [4] permitted the determination of the accommodation coefficient only on the surfaces of materials transparent to IR radiation. The circle of molecules investigated by such a procedure was also limited by the low sensitivity of the method, connected with the use of polychromatic radiation as the excitation source.

In the present work a method is developed for determining the coefficients of accommodation of vibrational energy of polyatomic molecules on a solid surface based on measurement of the pressure in a nonequilibrium rarefied gas absorbing laser radiation. The quantity ε was determined from a comparison between experimental data and the results of a theoretical analysis including the successive allowance for processes of laser excitation of gas molecules, their diffusion to the surface of the cuvette wall, and the relaxation of vibrational energy of the molecules in the volume and at the wall, as well as for the spatial distribution of the intensity of laser radiation and the temperature jump at the wall.

2. Experiment

The effect of a pressure change was investigated on an installation including a tunable CO_2 laser, a scanning device for measuring the radial distribution of radiation intensity, a cuvette containing the investigated gas and with a copper foil, with a Pt layer deposited on it, inserted into the cuvette tight against the wall, a differential micromanometer of the capacitance type with a sensitivity of $6.7 \cdot 10^{-4}$ Pa/Hz, the sensor of which was connected to the oscillatory loop of an LC oscillator, and systems for evacuating and admitting the gas and monitoring the radiation power. The experiments were carried out in SF_6, NH_3, and C_2H_4 gases in the pressure range of 15-400 Pa, when the condition $\lambda/R_c \leq 0.1$ is satisfied (λ is the mean free path of a molecule and $R_c \leq$ is the radius of the cuvette), while the quantity Δp

depends on ε. The indicated molecules were excited, respectively, by radiation of the P(30) line of the 10.6-μm band and the R(30) and P(10) lines of the 10.6-μm band of a CO_2 laser with a power of 0.2 W. The lines of laser radiation were identified by measuring the absorption in these gases on different vibrational—rotational transitions and comparing the data obtained with the results of [5]. The value of Δp in a gas absorbing radiation was determined from the detuning of the frequency of the LC oscillator in repeated measurements (with a frequency of 0.2 Hz) of the effect by a procedure eliminating the influence on Δp of gas leakage and non-steady adsorption. This procedure does not differ in principle from the procedure of measurement of the optoacoustic effect in a study of the process of V—T relaxation of excited molecules in a gas volume [6-8].

The change in gas pressure connected with the increase in gas temperature upon radiant heating of the entrance windows of the cuvette was established in additional tests and taken into account in the determination of Δp.

3. Theory of the Effect

The effect of a pressure change in a gas is analyzed in the form of the problem of the steady state of a spatially nonuniform rarefied gas — a mixture of excited and unexcited molecules. The state of such a gas will be determined by the balance of the rates of creation of vibrationally excited molecules (VEM) in the gas and their relaxation in the volume and at the wall, the diffusion of VEM to the wall, and the balance of heat fluxes arising as a result of V—T relaxation.

A system of equations of heat conduction and diffusion was used to describe the transfer processes in the gas. Here we assumed the condition n* ≪ n (n and n* are the numbers of molecules per cubic meter in the ground state and excited to the first vibrational level, respectively), which is satisfied for a gas absorbing low-intensity radiation ($J \leq 10^4$ W/m^2) [9] in the region of Knudsen numbers Kn = λ/R_c ≤ 0.1. The diffusion equation was solved with the boundary condition for n* determined by the balance of the fluxes of VEM incident on and reflected from the wall [1]. The coefficient of accommodation of vibrational energy (ε) appearing in such a boundary condition has the meaning of the probability of deactivation of an excited molecule in one collision with the wall. The radial distribution of radiation intensity required to solve the equation was assigned analytically in the form of a fourth-degree polynomial, describing the experimental data to within the experimental errors.

The heat-conduction equation was solved in the approximation of a temperature jump [10]. Here it was assumed, in accordance with [11], that the coefficient of accommodation of the translational energy of molecules is close to unity. From the solution of the system of equations we obtain the radial variations of the VEM concentration and the gas temperature, with the help of which the expression for the pressure change is found:

$$\Delta p = \frac{W_0 kp}{4\pi T \varkappa \left(1 + A\Omega_{VT}^{-1}\right)} \left\{ 1 - \frac{1}{4}\left(\frac{R_b}{R_c}\right)^2 + \frac{2}{R_c} d_0(p) - \frac{4}{\overline{R}_c} + \right.$$

$$\left. + \frac{96 R_b I_1\left(\overline{R}_b\right)}{R_b \overline{R}_b^4} \frac{\left[1 + \frac{4}{\overline{R}_b}\left(\frac{2}{\overline{R}_b} - \frac{I_0(\overline{R}_b)}{I_1(\overline{R}_b)}\right)\right]\left[1 + \left(\frac{2}{\overline{R}_c} - d_0(p)\frac{\overline{R}_c}{R_c}\right)f(\varepsilon, p)\right]}{I_1(\overline{R}_c) + f(\varepsilon, p)I_0(\overline{R}_c)} \right\} . \tag{3.1}$$

Here W_0 is the radiation power; k is the absorption coefficient; ϰ is the thermal conductivity of the gas; A is the Einstein coefficient; Ω_{VT}^{-1} is the V—T relaxation time; R_b is the beam radius, determined from the condition $J(R_b) = 0$; $I_0(\overline{R}_{b,c})$ and $I_1(\overline{R}_{b,c})$ are modified Bessel functions of zeroth and first orders, respectively. The functions $d_0(p)$, $f(\varepsilon, p)$, and $\overline{R}_{b,c}(p)$ are defined by the expressions

$$d_0(p) = \varkappa / [\rho c_V \langle V \rangle (\gamma + 1)],$$

$$f(\varepsilon, p) = \frac{\varepsilon \langle V \rangle}{2(2 - \varepsilon)\sqrt{(\Omega_{VT} + A)D^*}}, \quad \overline{R}_{b,c}(p) = \sqrt{\frac{(\Omega_{VT} + A)}{D^*}} R_{b,c}, \tag{3.2}$$

where D* is the coefficient of diffusion of VEM; ⟨V⟩ is the average thermal velocity of the molecules; $\gamma = c_p/c_V$ is the ratio of specific heats at constant pressure and constant volume; ρ is the gas density.

An analysis of the expression obtained for Δp showed that for $R_b \ll R_c$, $\Omega_{VT} \gg A$, and $D^*/R_c^2 \ll \Omega_{VT}$, when VEM do not reach the wall, this expression coincides with the well-known expression of [9]; the value of Δp does not depend on ε and is determined only by the pressure, the absorbed radiation power, and the temperature and thermal conductivity of the gas. In the general case, as follows from (3.1) and (3.2), Δp also depends on the VEM diffusion coefficient, the V—T relaxation time of the excited molecules, and on the coefficient of accommodation of vibrational energy, the temperature jump at the wall, the radial distribution of the radiation intensity, and the size of the cuvette.

The calculations showed that the temperature jump δT at the wall makes an important contribution to Δp (~15% for C_2H_4 at $p = 70$ Pa). In comparison with the case of gas heating by a heat flux through the cuvette wall, when $\delta T \sim p^{-1}$, the dependence $\delta T(p)$ has a fundamentally different character: $\delta T = $ const for $\Omega_{VT} \gg A$ and $D^*/R_c^2 \ll \Omega_{VT}$, while δT decreases with a decrease in pressure.

4. Determination of Accommodation Coefficients. Discussion of Results

In Fig. 1 we present the experimental data, as well as the results of a calculation of the dependence $\Delta p = \varphi(p)$, for the gases SF_6 and C_2H_4 (lines 1 and 2, respectively) obtained at $T = 295°K$. The analogous results of investigations in the gas NH_3 are presented in Fig. 2. The theoretical dependences were constructed with allowance for the influence of resonance V—V exchange of vibrational energy between molecules. Such exchange can result in different coefficients of diffusion of excited (D^*) and unexcited (D) molecules [1]. Estimates made from equations obtained in accordance with the results of [1] showed that the difference between D and D^* for SF_6 and C_2H_4 is less than 1%, while for NH_3 it is ~8%. The dependence $\Delta p = \varphi(p)$ was calculated in accordance with Eqs. (3.1) and (3.2), obtained for a two-level model. It is well known, however, that several vibrational modes are excited in SF_6 and C_2H_4 molecules as a result of rapid energy exchange between modes. We note that under such conditions, according to [10], vibrational modes with the lowest energies are the most likely to be excited. Therefore, the expression obtained for Δp can be used to investigate the effect of a pressure change in the indicated gases.

It is seen from Figs. 1 and 2 that the experimental data coincide with the theoretical dependences at high pressure, when the relation $(\Omega_{VT} + A(R_c^2/D^* \gg 1$ is satisfied. Control tests using cuvettes with different inside diameters and different laser-beam geometries showed that in this case Δp varies in accordance with the results of a calculation by Eqs. (3.1) and (3.2), indicating the correctness of the theoretical description of the pressure-change effect obtained. As the pressure decreases the experimental points in Figs. 1 and 2 do not coincide with the curves of the dependence $\Delta p = \varphi(p)$ for $\varepsilon = 0$ and 1 (dashed and solid lines, respectively). It was established that the experimental data are described by the expression obtained for Δp in the entire region of investigated pressures for the following values of ε: 0.29 ± 0.07 (NH_3), 0.8 ± 0.2 (SF_6), and 0.16 ± 0.06 (C_2H_4). The coefficients of accommodation of vibrational energy of ethylene molecules at $T = 327$ and $407°K$ were determined similarly ($\varepsilon = 0.13 \pm 0.02$ and 0.10 ± 0.04, respectively).

These errors in the quantity ε were determined as follows. Curves with variation of ε were calculated describing, within the experimental errors, the set of experimental values of Δp obtained at different pressures (the sizes of the symbols in Figs. 1 and 2 correspond to the errors in the measurements of Δp and p).

An analysis of the errors in the values of ε found showed that the inaccuracy in measuring Δp makes the main contribution. The errors in measuring Δp are connected with the frequency instability of the LC oscillator (± 2 Hz). With the use of the procedure of multiple repetition of measurements (10–15 times) of the effect at each value of p, this error was $\pm 0.65 \cdot 10^{-4}$ Pa. At the same time, the instability of the frequency of the laser radiation led to variation of the absorption coefficient of the gas molecules over the time of the experiment ($\Delta k/k \le 0.1$). The corresponding error, averaging over several measurements, was $(0.3-0.7) \cdot 10^{-3}$ Pa. We note that according to Fig. 3, where we present the dependence of Δp on ε obtained in accordance with (3.1) for ethylene at $p = 60$ Pa, when $\lambda/R_c \approx 0.1$ and $T = 298°K$, the method described proves to be the most sensitive to the determination of small values of ε (≤ 0.1). In this case as ε varies from 0 to 0.1 the quantity Δp varies in the range of $(7.5-4.5) \cdot 10^{-3}$ Pa. And measurements of ε in the range of $0.1 < \varepsilon \le 1$ requires a high accuracy in measuring Δp. For example, a determination of $\varepsilon = 0.8$ to within 10% requires a sensitivity of pressure change of no worse than $2 \cdot 10^{-5}$ Pa.
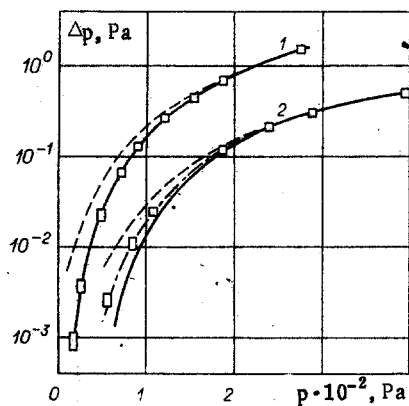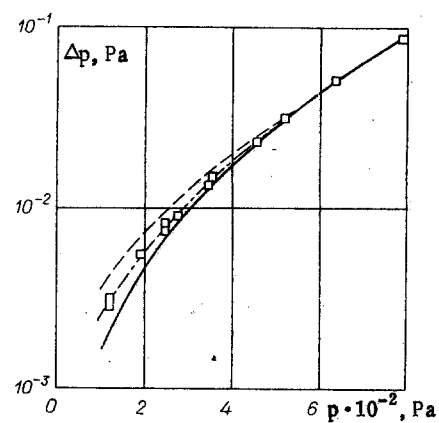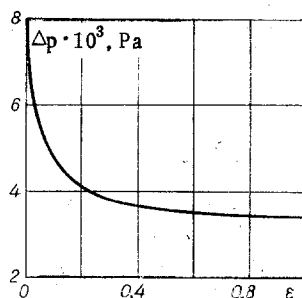
Fig. 1

Fig. 2

Fig. 3

From the results presented it follows that ε decreases with an increase in temperature for the C_2H_4 system. The dependence of ε on T is consistent with data known for other systems [1].

According to [11], the probability of heterogeneous relaxation of VEM should depend on the amount of energy E liberated in this process, as well as on the dipole moment μ of the radiative transition of the relaxing molecule. The pronounced difference in the values of the coefficients of accommodation of vibrational energy of the investigated molecules is evidently connected with this. The maximum value of ε occurs in SF_6 in the relaxation of the energy of vibrations of the ν_6 mode ($E \simeq 0.7 \cdot 10^{-20}$ J). For the gases C_2H_4 and NH_3 the values of E are higher and comprise $1.6 \cdot 10^{-20}$ and $2.1 \cdot 10^{-20}$ J, respectively. Despite the fact that $E_{C_2H_4} < E_{NH_3}$, we have $\varepsilon_{NH_3} > \varepsilon_{C_2H_4}$. This can be explained by the considerable difference in the dipole moments of the radiative transitions of these molecules ($\mu_{NH_3} = 0.17$ D, $\mu_{C_2H_4} = 0.01$ D).

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NUMERICAL MODELING OF PROCESSES IN A RELAXING GAS DURING

THE RAPID APPLICATION OF ENERGY

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An important problem of gasdynamics is the investigation of nonsteady processes during the pulsed application of energy to a confined volume of gas. This problem arises, for example, in a study of various types of pulsed-periodic lasers (carbon-dioxide and carbon–monoxide electric-discharge lasers [1-4], exciplex [5], and chemical lasers [6]). The nonuniform character of gasdynamic disturbances is a consequence of the spatial nonuniformity of energy application, which is determined by two circumstances. First, the working volume of a laser usually occupies only part of the channel cross section [3, 7-9]. Second, in gas-discharge lasers the pumping nonuniformity is connected with the complicated character of the distributions of the parameters of the working gas and the electric field, as well as with processes near the electrodes [3, 4]. The nonuniformity of energy application can grow due to the mutual influence of gas heating and gasdynamic processes [1, 3], although this effect is important only in cases when the duration of a pumping pulse is not small compared with the characteristic gasdynamic time.

The determination of shock-wave loads on the channel walls and of the time variation of the uniformity of the working medium is of practical interest. The presence of density disturbances increases the divergence of the radiation [10], and this effect is the more pronounced, the shorter the wavelength. On the other hand, a local density decrease leads to the necessity of reducing the electric field strength, and hence the applied energy, to prevent arcing [4].

A number of papers have been devoted to the theoretical investigation of gasdynamic processes in a channel during rapid energy application, but one-dimensional problems have been considered in the majority of them [1, 11, 12]. In [8] a two-dimensional analysis was made in an acoustic approximation. At the same time, the gasdynamic disturbance cannot be considered as small in the early stages of the process, since the gas pressure can grow severalfold as a result of pumping [4, 5]. The two-dimensional Euler equations are integrated in [3], but since the authors were interested in the influence of gasdynamics on the stability of the discharge, the calculation ends with the end of the pumping pulse (the shock waves have not yet reached the channel walls by this time). In all these investigations a gas with a constant ratio of heat capacities was considered as the working medium. Such a simplification is not always justified: In a carbon-monoxide electric-discharge laser, e.g., the energy stored in vibrational degrees of freedom can exceed the energy of the translational degrees of freedom. In this case, obviously, one must calculate the gas flow with allowance for vibrational relaxation.

We note that the characteristic Reynolds numbers are large in the problem under consideration, and hence the influence of dissipation on the gas dynamics of the flow can be neglected (at least in the initial stage of the process.

1. The purpose of this work is to investigate the influence of various physical effects on the gasdynamic processes in a channel during the rapid application of energy. Usually the