$$\omega_1^2 = \omega_p^2 + 2\beta^2 \frac{k^2c^2}{\omega_0^2}\omega_p^2, \quad \omega_2^2 = \Omega^2 + \omega_m^2. \tag{9}$$

It follows from (9) that the oscillations of the AMP in these cases are stable. This is of interest as an occurrence of suppression of instability in an AMP by an external field, where the increment was

$$\gamma = |\omega_m|/2,$$

as follows from (2) for $\omega_p^2 + k^2c^2 \sim \Omega$, where this increment occurs in the absence of an external field [5]. However, the conclusion is not general and applies only for the above conditions.

I am indebted to N. L. Tsintsadze for advice and valuable discussions.

LITERATURE CITED

1. N. G. Basov, É. M. Belenov, V. A. Danilychev, and A. F. Suchkov, "Electrical-ionization lasers with compressed carbon dioxide," Usp. Fiz. Nauk, 114, 213 (1974).
2. S. I. Krasheninnikov and V. V. Starykh, "A feature of the beam instability in a weakly ionized plasma of high density," Fiz. Plazmy, No. 3 (1977).
3. N. L. Tsintsadze and H. Wilhelmsson, "Instabilities in active molecular plasma," Phys. Scripta II, 11, No. 3 (1975).
4. O. E. H. Rydbeck and Å. Hjalmarsson, "Wave propagation properties of the molecular electronic plasma," Pennsylvania State Univ. Scientific Report No. 359 (1970).
5. V. P. Kovtun and N. L. Tsintsadze, "Electromagnetic-wave instability in an active molecular medium," Soobshch. Akad. Nauk Gruz. SSR, 86, No. 2 (1977).
6. V. P. Silin, Parametric Action of High-Power Radiation on Plasma [in Russian], Nauka, Moscow (1973).

RELAXATION OF MOLECULE VIBRATIONAL ENERGY IN HETEROGENEOUS MIXTURES

V. N. Faizulaev

UDC 539.196:541.182.2/3

In connection with the problem of producing low-temperature gasdynamic lasers (GDL) and proposals on the use of aerosol particles in the active media of GDL [1-3], investigations of the relaxation processes in vibrational nonequilibrium disperse systems are of great interest. The fundamental regularities of molecule vibrational relaxation in such systems were clarified in [3]. However, the singularities in the progress of the V—T and V—V' processes with the participation of adsorbed molecules were not considered here. The purpose of this paper is a more complete description of the kinetics of these processes and of heterogeneous vibrational relaxation of molecules as a whole [4].

Let a disperse system be a mixture of monomers of two species A_1, A_2 and complexes of identical magnitude (A_L) consisting of m_L molecules of the same species as A_2. The composition and other governing parameters of the heterogeneous mixture will be considered constant. We shall neglect the mutual interaction between the complexes. This is allowable if the mutual collision frequency of the complexes Z_{LL} in a two-phase system is much less than their collision frequencies with the monomers Z_{Ln} ($n = 1, 2$), i.e.,

$$\frac{Z_{LL}}{Z_{Ln}} \sim 4\sqrt{2}\, m_L^{-3/2} \frac{\varkappa_L}{\varkappa_n} \ll 1, \tag{1}$$

where $\varkappa_m$ is the relative molecule concentration of the m-component in the mixture. We shall consider monomer interaction with complexes under the assumption that the particle size and the mean spacing between them are small compared to the monomer mean free path in a gas.

Moscow. Translated from Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, No. 1, pp. 74-81, January-February, 1981. Original article submitted November 20, 1979.

In these approximations the description of molecule vibrational relaxation in a disperse system turns out to be quite similar to that usually used in the case of homogeneous mixtures. The main distinction is that the vibrational energy exchange between different components in heterogeneous mixtures can be due to not only the transfer of quanta (V—V' process), but also of molecules (M—M' process). The possibility of molecular exchange is associated with the dynamical nature of the phase equilibrium between the components which are distinguished by the aggregate state but are identical over the molecule species. We shall call such components paired. In the heterogeneous mixture under consideration, the gas ($m = 2$) and condensed ($m = L$) components consisting of molecules of the species A_2 as well as the gas ($m = 1$) and adsorbed ($m = 0$) components consisting of molecules of the species A_1 are paired.

In describing the vibrational relaxation, we start from the assumption about the Boltzmann distribution of molecules (diatomic) over the vibrational levels. Then the initial equation of the balance of quanta for molecules of each of the components for V—T, V—V', and M—M' processes can be written as follows:

$$\frac{de_m}{dt} = -R_m(e_m - \bar{e}_m) - \sum_{n \neq m} R_{mn}[e_m(e_n + 1)\ \varphi_{mn} e_n(e_m + 1)] - r_{mn}(e_m - e_n), \tag{2}$$

where $e_m = (\exp(\omega_m/T_m) - 1)^{-1}$; $\varphi_{mn} = \exp((\omega_n - \omega_m)/T)$; ω_m, T_m are the frequency of the (natural) vibrations and the vibrational temperature of the m-component molecules; $\bar{e}_m$, value of e_m for $T_m = T$; R_m, R_{mn}, r_{mn}, rates of the elementary V—T, V—V', M—M' processes.

It is convenient to represent the expressions for R_m, R_{mn} in a form corresponding to the gas-kinetic treatment of molecule interaction in a heterogeneous mixture

$$R_m = Q_m + \sum_{n \neq m} \nu_{mn} P_m^{(n)}, \quad R_{mn} = \nu_{mn} P_{mn}^{(n)}, \tag{3}$$

where Q_m is the rate of the vibrational-translational relaxation of the m-component molecules during mutual interaction, $P_m^{(n)}$ and $P_{mn}^{(n)}$ or briefly $P_{m,n}^{(n)}$ is the mean probability of V—T or V—V' deactivation of m-component molecules during collisions with n-component molecules, and ν_{mn} is the collision frequency between m-component and n-component molecules. Here, according to the principle of detailed equilibrium

$$P_{mn}^{(n)} = \varphi_{nm} P_{nm}^{(m)}, \quad \frac{\nu_{mn}}{\nu_{nm}} = \frac{\varkappa_n}{\varkappa_m}. \tag{4}$$

However, it must be kept in mind that interaction between component molecules in different aggregate states in a heterogeneous mixture occurs on the surface rather than in the bulk, and therefore, can be inaccessible for part of the molecules. Hence, the quantities $P_{m,n}^{(n)}$ and ν_{mn} can only characterize the elementary process effectively in the general case by determining its velocity on the average for molecules of this component.

As an illustration, let us present the determination of these quantities for interaction between molecules of the condensed and adsorbed components and the gas molecules. Let the degree of covering of the complex surface by the adsorbed molecules be small, i.e.,

$$\theta \simeq \frac{\varkappa_0 m_L}{\varkappa_L m_L^{(S)}} \ll 1,$$

where $m_L^{(S)}$ is the number of molecules comprising the surface of the complex. Then the probability $P_{m,n}^{SC}$ computed in conformity with the shock mechanism of surface deactivation of the molecules [5, 6] can be taken as $P_{m,n}^{(n)}$. Here since

$$\nu_{1L} = Z_{1L}, \quad \nu_{10} = \theta Z_{1L},$$

according to (4)

$$\nu_{L1} = \frac{Z_{L1}}{m_L}, \quad \nu_{01} = \frac{Z_{L1}}{m_L^{(S)}}.$$

It has actually been taken into account here that although only one of the molecules of the complex is directly subjected to shock deactivation during monomer collision with a complex, they can all participate indirectly in this process. This is related to the presence of resonance vibrational exchange that sets up a uniform distribution of quanta within the complexes.

As regards the molecular exchange rates r_{mn}, in the case of paired gas and adsorbed components they are then determined as follows:

$$r_{10} = \xi_1 Z_{1L}, \quad r_{01} = (\tau_a)^{-1}, \tag{5}$$

where ξ_1, τ_a are the adhesion coefficient and the adsorption time of the gas molecules on the surface. The molecular exchange rates for the paired gas and condensed components are also given similarly. Here ξ and τ_a should be understood as quantities characterizing the molecule condensation and evaporation processes, respectively. For unpaired components evidently $r_{mn} = 0$.

Depending on the relationship between the rates of the V—T, V—V', and M—M' processes for the gas, adsorbed, and condensed components, different heterogeneous relaxation modes of the vibrational energy of the molecules are possible in a disperse system. Let us examine the most typical case when the rates of the processes mentioned turn out to be considerably higher for adsorbed molecules than for the others. The reason for this is their relatively low concentration in the mixture $\varkappa_0 \ll \varkappa_n$ ($n = 1, 2, L$), as well as the high efficiency of the surface deactivation mechanisms [5-7]. Under such conditions, the heterogeneous relaxation of molecules of the gas and condensed phases should proceed with a quasistationary balance of quanta for the adsorbed component. Hence, in a linear approximation

$$e_0 \simeq \tilde{e}_0 = \frac{1}{\tilde{R}_0}\left[R_0\bar{e}_0 + \sum_{n\neq 0}(R_{0n}\varphi_{0n} + r_{0n})\, e_n\right], \tag{6}$$

where

$$\tilde{R}_0 = R_0 + \sum_{n\neq 0} R'_{0n}, \quad R'_{0n} = R_{0n} + r_{0n}.$$

Taking account of (6) substantially simplifies the analysis of the kinetics of the V—T and V—V' processes proceeding with adsorbed molecule participation. Formally this is achieved by eliminating the equation for $m = 0$ from (2) and replacing the quantity e_0 by $\tilde{e}_0$ in the right sides of the remaining linearized equations. Executing such a procedure and neglecting the difference in the natural vibrations frequencies of molecules of the paired components, we have

$$\frac{de_m}{dt} = -K_m(e_m - \bar{e}_m) - \sum_{n\neq m} K_{mn}(e_m - \varphi_{mn}e_n), \tag{7}$$

where

$$K_m = R_m + R'_{m0}\frac{R_0}{\tilde{R}_0}, \quad K_{mn} = R'_{mn} + R'_{m0}\frac{R'_{0n}}{\tilde{R}_0} \qquad (m, n = 1, 2, L). \tag{8}$$

The first terms in the expressions for the rates of the heterogeneous V—T and V—V' relaxation of the gas and condensed phase molecules correspond to the V—T and V—V' processes due to the direct mutual interaction of these components, and the second to relaxation processes, proceeding with the participation of adsorbed molecules.

Let us discuss the qualitatively most interesting consequences of the results obtained that concern the adsorption mechanism of gas molecule deactivation. Usually kept in mind by this mechanism [5, 7] is a two-stage process for which the vibrational deactivation of gas molecules sets in because of adhesion to the surface and vibrational relaxation in the adsorbed state. In conformity with this, the adsorption component of the probability of surface V—T or V—V' deactivation of gas molecules is determined in the form

$$P^{Sa}_{1,L} = \xi_1^*\left(1 - \exp\left(-\tau_a^* R_{0,L}\right)\right), \tag{9}$$

where ξ_1^* and τ_a^* characterize the process of vibrationally excited molecule adsorption. In such a determination it is assumed that during adsorption the deactivated molecules does not succeed in transferring its excitation to gas phase molecules, i.e., $\tau_a R_{01} \ll 1$. In practice, this is possible at low pressures or relatively high temperatures since $\tau_a = \nu^{-1} \exp(U_S/T)$, where ν is the characteristic frequency of the intermolecular vibrations, and U_S is the adsorption energy.

The extraction of adsorbed molecules in the self-consistent component of a heterogeneous mixture with the appropriate inclusion of molecular and vibrational exchange in the considerations permits removing this constraint in describing the adsorption mechanism of gas molecule deactivation. This can be seen by the example of a kinetic relationship for $P^{Sa}_{1,L}$ that results directly from (8)

$$P^{Sa}_{1,L} = \frac{R'_{10}R_{0,L}}{Z_{1L}\tilde{R}_0}. \tag{10}$$

Let us expand this expression in the case of a one-component gas, when the adsorption deactivation process of the molecules A_1 can proceed either in the V–T channel, or because of vibrational exchange between the adsorbed molecules and the condensate molecules. Then by neglecting the corresponding terms in $\tilde{R}_0$ (R_{0L} for the V–T, and R_0 for the V–V' process), and taking into account that in the state of phase equilibrium between the paired gas and adsorbed components

$$\frac{R_{10}}{R_{01}} = \frac{\varkappa_0}{\varkappa_1} = \frac{r_{10}}{r_{01}},$$

we have

$$P^{Sa}_{1,L} = \xi_1 \frac{\tau_a R_{0,L}}{1 + \dfrac{\tau_a R_{0,L}}{1 + \tau_a R_{01}}}. \tag{11}$$

It hence follows that for $\tau_a R_{01} \ll 1$ (low pressure) the kinetic definition (10) is adequate (9). Otherwise, it does not correspond to (9) and describes the so-called exchange mechanism of adsorption deactivation of the gas molecules [7], which is realized at high pressures or low temperatures. However, it turns out that if ξ^*_1 in (9) is understood to be the quantity θP^{SC}_{10}, and τ^*_a is $(R_{01})^{-1}$, respectively, then it can correctly describe this case also. Actually, this means that the sense of characteristics of the adsorption process for quanta rather than molecules is attributed to the parameters ξ^*_1 and τ^*_a in (9). The adsorption mechanism is hence treated as a two-stage process for which the vibrational deactivation of the gas molecules sets in because of adhesion and the destruction of quanta during their adsorption on the surface. Analysis shows that such a treatment turns out to be valid even in the general case when delivery of vibrational gas molecule excitation on the surface can be due both to the transfer of quanta to the adsorbed molecules and to adhesion of the excited molecules. Then, the quantity

$$\xi^*_1 = \xi_1 + \theta P^{SC}_{10} \tag{12}$$

should be taken as the quantum adhesion factor in (9), and

$$\tau^*_a = \frac{\tau_a}{1 + \tau_a R_{01}} \tag{13}$$

as adsorption time.

Let us continue to analyze the kinetics of heterogeneous relaxation of molecules in a disperse system. We spend the main attention here on the singularities of the catalytic action of aerosol particles on the relaxation processes in the gas [3, 6]. As an illustration we examine the case of a small condensate impurity when the quasistationary balance of the quanta is realized not only for the adsorbed but also for the condensed component. Then the equations (7) of heterogeneous gas molecule relaxation can be reduced to the following form:

$$\frac{de_m}{dt} = -\Gamma_m\left(e_m - \bar{e}_m\right) - \Gamma_{mn}\left(e_m - \varphi_{mn}e_n\right), \tag{14}$$

where

$$\Gamma_{m,n} = K_{m,n} + K_{mL}\beta_{L,n}, \quad \beta_{L,n} = \frac{K_{L,n}}{K_L + \sum\limits_{n \neq L} K_{Ln}} \quad (m, n = 1, 2). \tag{15}$$

The first term in the relationship obtained for $\Gamma_{m,n}$ corresponds to heterogeneous V–T or V–V' relaxation proceeding over the forward channel, and the second term over the exchange channel through condensate molecules.

Let us clarify how effective is the action of both channels of the catalytic effect of the aerosol particles on the vibrational–translational relaxation of the gas molecules. Let the condensate particles consist of molecules of the same species as the gas, and let them be spherical drops of the identical volume $m_L b$, where $b = (2/3)\pi d^3$ is the intrinsic volume of the molecules in the fluid, and d is the molecule gas-kinetic diameter. Then the expression for the component Γ_1 corresponding to the forward channel of heterogeneous V—T relaxation can be represented in the form

$$\Gamma_1^{VT} = \varkappa_L N k_1^S, \tag{16}$$

where

$$k_1^S = \frac{Z_{1L} P_1^S}{\varkappa_L N} = \pi d^2 v P_1^S \frac{\left(1 + \sqrt[3]{4m_L}\right)^2}{4\sqrt{2}\, m_L} \tag{17}$$

is a rate constant; P_1^S, probability of surface V—T deactivation of the gas molecules; and N, v, total concentration and the thermal velocity of the molecule mixture. The exchange component of Γ_1 can be represented analogously:

$$\Gamma_1^{VV'T} = \varkappa_L N k_{1L}^S \beta_L. \tag{18}$$

The quantity β_L has the meaning of the probability of quantum destruction during a one-time residence in the condensate particle. As a function of the size of the complex for $m_L \gg 1$, when $\nu_{L1} \simeq \nu_{11}/(2\sqrt[3]{m_L})$, it can be defined as follows:

$$\beta_L \simeq \left(1 + \sqrt[3]{\frac{m_*}{m_L}}\right)^{-1}, \tag{19}$$

where

$$m_* \simeq \left(\frac{\nu_{11} P_{L1}^S}{2Q_L}\right)^3. \tag{20}$$

Here it has been taken into account that the rate of vibrational—translational molecule relaxation in the liquid phase particles can be considered independent of their dimension m_L and equal to Q_L. In this approximation

$$\Gamma_1^{VV'T} \simeq \varkappa_L Q_L \left(1 + \sqrt[3]{\frac{m_L}{m_*}}\right)^{-1}. \tag{21}$$

The form of the dependence of $\Gamma_1^{VV'T}$ on m_L is due to the competition between two factors. On the one hand, the intensity of vibrational exchange between the gas and condensed components decreases as m_L increases, and on the other hand the probability of destruction of quanta in condensate particles grows. Although the dimension of the particles is small compared to m_*, the action of both factors is compensated completely and hence, the velocity of heterogeneous gas molecule relaxation over the exchange channel turns out to be independent of the disperseness of a two-phase system. With the passage into the domain $m_L > m_*$, where exchange deactivation of gas molecules in the complex acquires an irreversible nature ($\beta_L = 1$) (as in the case of macroscopic particles), the efficiency of this relaxation channel starts to be reduced in conformity with the dependence of k_{1L}^S on m_L

Let us present a comparative estimate of the efficiency of both channels of heterogeneous V—T relaxation of the gas molecules. Since direct V—T deactivation of the gas molecules on the intrinsic condensate particles can be due to just the shock mechanism, then according to its simplest model [5]

$$\frac{P_1^S}{P_1^0} \simeq \exp\left(\frac{D_S - D_0}{T}\right),$$

where D_S and D_0 are the depths of the potentials of (shock) interaction of molecules on the surface and in the gas phase. Setting $D_S = 4D_0$, we obtain that $P_1^S/P_1^0 = 3 \cdot 10^2$ for the CO_2 molecule, say, for $D_0 = 190$°K and $T = 100$°K. For such a difference between the probabilities of surface and volume V—T deactivation of the gas molecules, the ratio between the appropriate relaxation rates is $\Gamma_1^{VT}/\Gamma_1(0) \simeq 5$ for $\varkappa_L = 0.1$, $m_L = 10^2$. If the exchange channel of surface deactivation is included, then the catalytic action of the condensate particles on the vibrational—translational relaxation of the gas molecules can be expressed much more strongly. Thus, if it is considered that vibrational relaxation of the molecules in the condensate particles occurs with a velocity Q_L, corresponding to the mechanism of binary collisions in a fluid [8, 9], then the quantity $\Gamma_1^{VV'T}/\Gamma_1(0)$ for the deformation vibrations of CO_2, say, is 10^3 for $N = 10^{18}$ cm^{-3} ($m_* \sim 10^3$) and the above-mentioned aerosol parameters.

In addition to the V—T processes, the aerosol particles can also accelerate the vibrational exchange in the gas [3]. This effect is achieved because of the intervention of the aerosol particles during the vibrational exchange between gas molecules. Let us examine it in more detail under conditions when the narrowest place in the vibrational exchange over the A_1—(A_L)—A_2 channel is the quantum transfer process between the molecules A_1 and A_L. This case is most typical when using aerosol particles as catalyst of nonresonance pumping in GDL in which the molecules A_2 are the energy carrier and A_1 is the radiating element of the active medium.

Let the external parameters (mass, diameter) of the mixture molecules be identical. Then by considering that the fraction of condensate of the component A_2 is small ($q = \varkappa_L/\varkappa_2 \ll 1$), we obtain according to (15)

$$\frac{\Gamma_{12}(q)}{\Gamma_{12}(0)} \simeq 1 - q + \frac{q}{2\sqrt[3]{m_L}} \frac{P_{1L}^S}{P_{12}^0}(1 - \beta_L). \qquad (22)$$

It is hence seen that the smaller the size of the condensate particles, the more strongly should the catalytic effect by expressed. Where this is due not only to an increase in the vibrational exchange rate between molecules of the gaseous and condensed phases, but also to the diminution in the probability of quantum destruction during their transfer over the heterogeneous channel. If $m_L \ll m_*$, then quantum leakage because of relaxation losses in the condensate particles can be neglected. In this case, the catalytic action of the aerosol on the vibrational exchange in the gas turns out to be approximately the same as on the direct V—T relaxation of the molecules A_1.

Let us present a quantitative estimate of the catalytic action of the aerosol on the vibrational exchange in a mixture $CO_2(1)$—$O_2(2)$, in which the O_2 molecules are the vibrational energy carrier for the paired (deformation and symmetric) modes of the CO_2. This example is of interest in connection with the possibility of producing a gasdynamic CO_2 laser at the transition (03^10)—(10^00) [10, 11]. Considering the adsorption mechanism of V—V' deactivation responsible for the vibrational exchange between the CO_2 molecules and the O_2 condensate particles ($\omega_2 - \omega_1 \approx 270$°K), and estimating $R_{\circ L}$ in (11) in the approximation of binary molecule collisions in a fluid with $\nu_{\circ L} = \nu$, we obtain that if $\xi_1 = 1$, $U_S = 6D_0$ ($D_0 = \sqrt{D_0(1)D_0(2)} = 155$°K), then the quantity P_{1L}^S/P_{12}^0 is $3 \cdot 10^3$ for $T = 100$°K ($P_{21}^0 = 10^{-5}$ [12]) and $\Gamma_{12}/\Gamma_{12}(0)$ is, respectively, 10 for $q = 0.03$, $m_L = 10^2$. It is essential that such an acceleration of vibrational exchange be possible in the background of a low level of quantum relaxation losses in the condensate particles $\beta_L \ll 1$. This is related to the low velocity of natural vibration damping of O_2 in the liquid phase ($Q_L \sim 10^2$ sec^{-1} [13]), and more exactly, to the large critical size, for them, of the condensate particles m_*. Thus, for $N_1 = 10^{18}$ cm^{-3} it can be $m_* \sim 10^{13}$, and the corresponding relaxational losses for the above-mentioned disperseness of the condensate is on the order of 10^{-4} of the CO_2 molecule pumping power over the heterogeneous V—V' exchange channel with O_2. This circumstance affords the possibility of effective utilization of the O_2 aerosol as not only a nonresonance pumping catalyst, but also an energy carrier of the active medium of a CO_2—GDL in paired modes.

The author is grateful to V. K. Konyukhov for constant attention to the research and for useful remarks.

LITERATURE CITED

1. V. K. Konyukhov and A. M. Prokhorov, "On the possibility of producing an adsorption-gasdynamic quantum generator," Pisma Zh. Eksp. Teor. Fiz., 13, No. 4 (1971).
2. A. S. Biryukov, V. M. Marchenko, and A. M. Prokhorov, "Population inversion of vibrational levels in the mixing of streams of nonequilibrium nitrogen and a carbon dioxide aerosol," Zh. Eksp. Teor. Fiz., 71, No. 5(11) (1976).
3. V. K. Konyukhov and V. N. Faizulaev, "Kinetics of vibrational relaxation of molecules in gas-aerosol systems, and lasers using two-phase media," Kvantovaya Elektron., 5, No. 7 (1978).
4. V. N. Faizulaev, "On vibrational energy relaxation of molecules in heterogeneous mixtures," Preprint No. 128, Phys. Inst. Acad. Sci. USSR (1979).
5. T. F. Hunter, "Vibrational energy transfer at gas-solid interfaces," J. Chem. Phys., 51, No. 6 (1969).
6. V. K. Konyukhov and V. N. Faizulaev, "On the influence of gas condensation on the rate of relaxation processes in gasdynamic lasers," Kvantovaya Elektron., 1, No. 12 (1974).
7. Yu. M. Gershenzon, V. B. Rozenshtein, and S. Ya. Umanskii, "Heterogeneous vibrational relaxation of N_2, CO_2, and N_2O molecules," Prob. Kinetiki Katal., 17, 36 (1978).

8. W. M. Madigosky and T. A. Litovitz, "Mean free path and ultrasonic vibrational relaxation in liquid and dense gas," J. Chem. Phys., 34, No. 2 (1961).
9. B. F. Gordiets, Sh. S. Mamedov, and L. A. Shelepin, "Vibrational relaxation and lasers using intermolecular transitions in fluids and molecular crystals," Zh. Eksp. Teor. Fiz., 69, No. 8 (1975).
10. V. K. Konyukhov and V. N. Faizulaev, "On the possibility of producing a gasdynamic laser at transitions between levels of paired CO_2 modes," Kvantovaya Elektron., 5, No. 12 (1978); FIAN Preprint No. 204, Phys. Inst. Acad. Sci. USSR (1978).
11. A. A. Vedeneev, A. Yu. Vol'kov, et al., "Gasdynamic laser with thermal pumping at transitions between deformation and symmetric modes of CO_2," Pisma Zh. Tekh. Fiz., 4, No. 11 (1978).
12. H. E. Bass, "Vbirational relaxation in CO_2/O_2 mixtures," J. Chem. Phys., 58, No. 11 (1973).
13. W. F. Calaway and G. E. Ewing, "Vibrational relaxation of small molecules in the liquid phase: liquid nitrogen doped O_2, CO_2, and CH_4," J. Chem. Phys., 63, 2842 (1975).

KINETICS OF DIMER FORMATION IN RAREFIED WATER VAPOR STREAMS

A. A. Vigasin

UDC 533.72;533.6.01.8

Processes of the formation of small associates, and in particular, of water molecule dimerization continue to attract the attention of specialists in different areas of science and its applications. Such processes are examined, e.g., in the construction of kinetic models of vapor condensation [1]; the representation of water molecule dimerization aids in the intepretation of the passage of IR radiation in the transparency windows of the atmosphere [2]. Preliminary estimates are made in [3] of the possibility of producing a gasdynamic condense-laser that uses the energy of vibrational excitation of dimers formed during the escape of low-density water vapor from a nozzle. A study of different aspects of the spectral and physicochemical phenomena of molecule associations under equilibrium and nonequilibrium conditions requires further refinement of the molecular parameters of associates, perfection of methods to determine these parameters, and construction of kinetic models of associate formation.

A number of papers have recently appeared on studying associates in molecular and gasdynamic beams of different gases [4-6], including water vapor [4, 6]. Results of mass spectral measurements of nonequilibrium concentrations of water dimers during the escape of rarefied vapor into a vacuum are presented in [6]. The dimer-formation model proposed in [6] permitted the author to describe the experimental results he obtained about dimer concentrations in a stream with sufficiently high accuracy. The principal statement in the construction of the kinetic model [6] is the use of the temperature dependence of the equilibrium dimer concentration $\xi_{2e}(T)$ obtained earlier [7] by a computation of part of the second virial coefficient (SVC) of the vapor that corresponds to the bound and metastable states of the molecules. An attempt is made in this paper to relate nonequilibrium dimer concentrations directly to molecular parameters, whereupon the range of applicability of the kinetic model might be extended significantly.

Considerable cooling is achieved in the supersonic escape of a rarefied gas into an evacuated space; the translational temperature in the stream can be several tens of degrees Kelvin, for instance. Intensive molecule dimerization occurs in the initial stage of the cooling because of two- and three-particle monomer collisions:

$$M+M\rightleftarrows D^*; \tag{1}$$

$$M+M+M\rightleftarrows D+M. \tag{2}$$

The reactions (1) and (2) are reversible and each is characterized by its own rate of direct (formation) K_f and reverse (dissociation) K_d processes. Only vibrationally excited molecules with a complete store of vibrational energy $\varepsilon_K \gtrsim \varepsilon_D$ (ε_D is the dimer molecule dissociation

---

Moscow. Translated from Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, No. 1, pp. 81-87, January-February, 1981. Original article submitted September 24, 1979.

0021-8944/81/2201-0066$07.50