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SPATIAL DISTRIBUTION OF CO₂ DIMERS IN
 AXISYMMETRIC GAS JETS EXPANDING IN A VACUUM

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The condensation of molecular gases in engines and in laser and gas-dynamical equipment has attracted the attention of researchers for decades. However the capability of gases expanding in a vacuum to associate has been actively used only in recent years to study the earliest stages of this process and the weak molecular interactions leading to the formation of van der Waals or hydrogen-bonded complexes. These studies were based on special methods of microwave and optical spectroscopy. The use of spectroscopic methods in combination with the gas-dynamical method of generating molecular complexes has been used to obtain extensive information on the structure and properties of complexes (see [1], for example). But the further development and increased sensitivity of the spectroscopic methods of probing gas flows requires in many cases a more detailed theoretical description of the physical and chemical processes in nonequilibrium moving media. In particular, for experiments designed to obtain spectra of molecular complexes of certain compositions and sizes, a careful consideration of the optimal choice of the geometrical and other parameters is usually necessary.

The kinetics of the initial stages of the condensation—dimerization of molecular gases such as water vapor and carbon dioxide has been studied by several authors [2-7]. However these studies were concerned mainly with determining the dependence of the steady-state concentration of dimers in a molecular beam on the parameters in the mixing chamber and on the nozzle diameter. The fraction of dimers was measured in [2-4] with a mass spectrometer and the composition of the gas was controlled only along the direction of propagation of the molecular beam.

Spectroscopic studies of the rotational and vibrational—rotational transitions of complexes are usually carried out under conditions such that the probing beam (or beams) of electromagnetic radiation pass through a jet of freely expanding gas in the direction perpendicular to the symmetry axis of the jet. This geometry is also typical of the widely-used method of microwave Fourier spectroscopy, and in the study of infrared absorption and spontaneous and coherent anti-Stokes Raman scattering [1]. In the design of experiments of this kind it is desired to have an idea of the spatial distribution of dimers in the expanding

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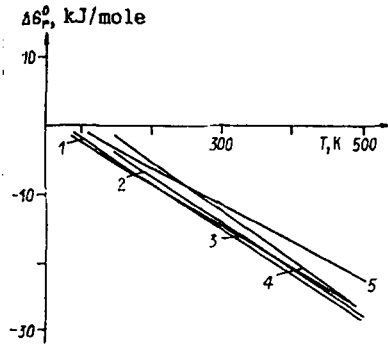


Fig. 1

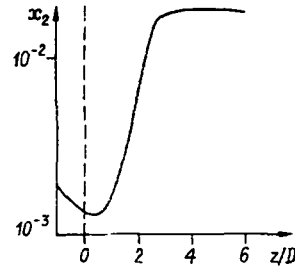


Fig. 2

gas jet, as well as the characteristic spatial scales of the concentration and the localization of maximum concentration of dimers. In the present paper we discuss the results of calculations of the two-dimensional concentration field of CO₂ dimers for expansion of pure CO₂ gas or a mixture of CO₂ with Ar into a vacuum from an axisymmetric aperture.

1. Kinetic Model. There are several models in the literature describing the kinetics of dimerization [2-7]. One group of models [2, 3, 7] is constructed on the basis of the assumption that dimers D are formed as a result of three-particle collisions



where the monomer M can serve as the particle A. The rate constant k_f of the direct reaction (1.1) can then be estimated as the frequency of trinary collisions, while the rate constant of the reverse reaction k_d can be found in terms of the equilibrium constant K_e from the formula

$$k_d = K_f K_e / kT \quad (1.2)$$

(k is the Boltzmann constant and T is the temperature).

In many cases, such as the kinetics of dimerization of water vapor [3], this model accurately describes the experimental data. But there is evidence that the model is not sufficiently rigorous at low pressures for dimers of water [6] and also for an inert gas such as argon [7].

Another group of kinetic models starts from the assumption that the dimer dissociation reaction goes through two stages which are widely separated in time. In the first stage there is collisional activation of stable dimers



and in the second there is a spontaneous dissociation of the molecule D^* , which is excited above the dissociation threshold in the reaction (1.3):



The reactions (1.3) and (1.4) are reversible and therefore the total process can be written formally in the form (1.1). It is significant that at low pressure the rate of dissociation of particles D is determined by the rate of activation in the reaction (1.3). Without dwelling further on the description of the different possible methods of determining the rate constants of the reactions (1.3) and (1.4), we note that one of the most obvious methods is the use of the following known expression [8] for the rate constant k_d in the limit of low pressure:

$$k_d = PZ_c \Gamma(s, m) / \Gamma(s) = PZ_c \exp(-m) \sum_{i=0}^{s-1} \frac{m^i}{i!}. \quad (1.5)$$

Here s is the number of active degrees of freedom; $m = D_e/kT$; D_e is the binding energy of the complex; Z_c is the number of strong collisions in the reaction (1.3); P is a factor describing the effectiveness of the collision, which will be treated below as an adjustable parameter; $\Gamma(s, m)$ and $\Gamma(s)$ are the incomplete and complete gamma functions, respectively.

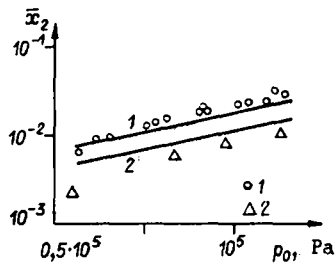


Fig. 3

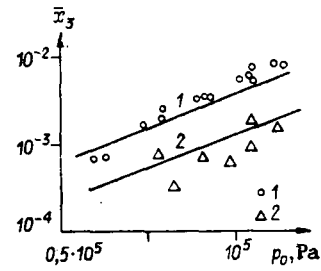


Fig. 4

We will assume that s is equal to the number of intermolecular vibrational degrees of freedom, and that Z_c is given by

$$Z_c = [(d_1 + d_2)/2]^2 \left[8\pi kT \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \right]^{1/2}, \quad (1.6)$$

where d_1 , d_2 and m_1 , m_2 are the kinetic diameters and masses of the colliding particles.

Equation (1.2) can be used to express K_f in terms of the constant K_d given by (1.5) and the equilibrium constant K_e . The latter can be found by computing the partition functions with respect to the molecular parameters of the monomers and dimers. Hence a limited number of molecular constants is sufficient to determine the kinetic constants. For many bimolecular complexes, such as CO_2 dimers, these constants are known either experimentally or from quantum-chemical calculations [1].

The kinetic equations can be written down for two reactions of the form (1.1), in which $(\text{CO}_2)_2$ dimers dissociate as a result of collisions with CO_2 monomers or with argon. The equations have the form

$$\frac{dc_D}{dt} = -K'_d c_D c_M \rho + K'_f c_M^3 \rho^2, \quad \frac{dc_D}{dt} = -K_d c_D c_A \rho + K_f c_M^2 c_A \rho^2. \quad (1.7)$$

Here $c_i = x_i/\mu$ is the molar-mass fraction; x_i is the molar concentration of the i -th component; μ is the mean molecular mass; ρ is the density of the mixture.

The concentrations c_i in the jet are determined by integrating (1.7) numerically using the Geer method [9] together with the gas-dynamical equations for one-dimensional flow. The temperature distributions $T(i)$ along the streamlines were assumed to be given. This approach cannot take into account the combined effect of the kinetics and gas dynamics; however the small degree of association under the conditions considered here makes this approximation valid.

2. Gas Dynamics of Jets. Data on the spatial dependence of the Mach number M along different streamlines are necessary in order to describe the field of the gas-dynamical variables in the isentropic approximation. Furthermore, from the known relations of [10], one can find the temperature T/T_0 , density ρ/ρ_0 , and the other parameters divided by their values in a gas at rest for the case of constant adiabatic exponent γ . For points on the axis of the jet such that $z/D > 1$ (D is the critical cross-section diameter) the analytical approximation for M developed in [11] is widely used. Since the initial conditions on (1.7) (the equilibrium values of the concentrations) refer to a gas at rest, the approximation $M(z/D)$ must be supplemented by the value of M for at least two points: $M(0) = 1$ and $M(-1) = 0$. Thus it was assumed that the gas is at rest at distance D from the aperture inside the chamber, and that the velocity of the gas upon exit from the chamber is equal to the speed of sound. Values of M between these two points were calculated by linear interpolation. Values of M for the other streamlines were calculated in the same way. Here, however, in view of the absence of an analytical formula of the Ashkenas-Sherman type, we had to resort to linear interpolation between all of the tabulated values of $M(z/D, y/D)$ in [10] for $\gamma = 1.67$ (small impurity of CO_2 in Ar) and $\gamma = 1.4$ (pure CO_2).

Having the field of values of M at constant γ , it is not difficult to obtain the corresponding values of the temperature and density along the streamlines for mass flow rates of the gas from 0 to 0.8. The dependence of the temperature $T(L)$ (L is the distance from the virtual source) was then used in finding the solution of the kinetic equations (1.7) and the dependence of the density on the coordinates was used in the calculation of the volumetric concentration of the dimers.

3. Choice of the Parameters and Results of the Calculations. The constant K_e of the equilibrium dimerization reaction is usually found with the help of the expressions found by Stogrin and Herschfelder for nonpolar and polar molecules [1]. These expressions were obtained from a classical calculation of the partition functions with respect to the bound and metastable states of molecular pairs, where the metastable states correspond to the formation of short-lifetime pairs rotating with respect to the common center of mass. We note that for polyatomic molecules there exist other channels of metastable pair formation involving a temporary transformation of the energy of dissociation into the energy of the internal vibrational or rotational degrees of freedom of the complex.

In the present paper the temperature dependence of the equilibrium constant K_e was expressed in terms of the same molecular constants as $K_d(T)$. It was assumed that CO_2 molecules form rigid dimers with symmetry C_{2h} . Linear CO_2 monomers were arranged parallel to one another at a separation of 0.311 nm and the distance between carbon atoms was 0.35 nm. Such a structure was found in [12] by analyzing the vibrational—rotational spectrum of the $\nu_1 + \nu_2$ band of $(\text{CO}_2)_2$ dimers, where the spectrum was obtained by the method of vibrational infrared predissociation of molecules in a freely expanding He jet. Other experimental data from IR and CARS spectroscopy of CO_2 dimers [13] also support this configuration, as well as the quantum-chemical calculations [14–16].

After calculations of the corresponding partition functions, the temperature dependence of K_e can be written in the form

$$K_e = \frac{T^3}{9.4Q_V} \exp(-D_0/kT), \quad (3.1)$$

where $D_0 = D_e - \frac{s}{2} h\bar{\nu}$ is the energy of dissociation, $\bar{\nu}$ is the mean frequency of intermolecular vibrations; h is Planck's constant; Q_V is the partition function of the s vibrations with frequency $\bar{\nu}$.

For convenience in comparing with the data in the literature, in Fig. 1 we show the temperature dependence of the increment in the Gibbs potential ΔG_r^0 , which is related to K_e by

$$\Delta G_r^0 = -RT \ln K_e. \quad (3.2)$$

In Fig. 1, curve 1 was constructed from (3.1) and (3.2) with $\bar{\nu} = 65^\circ\text{K}$, $D_0 = 650^\circ\text{K}$, $s = 4$, and curves 2, 3, 4, and 5 show the results of [2], [4], [17], and [18], respectively. We see that K_e calculated from (3.1) agrees closely with the data from independent sources.

The above values of the molecular parameters were used in (1.5) for K_d . To estimate the collision frequency we assumed that the collision diameters for Ar—Ar and CO_2 — CO_2 were 0.292 and 0.32 nm, respectively [19]. The effective collision diameters for the pairs $(\text{CO}_2)_2$ —Ar and $(\text{CO}_2)_2$ — CO_2 were taken to be 0.37 and 0.45 nm, respectively. The inaccuracy of these last values can be compensated for by choosing the parameter P in (1.5) such that the calculated steady-state concentration \bar{x}_2 of dimers on the axis of a pure CO_2 jet coincides with the mass-spectrometry measurements. In Fig. 2 we show the dependence of the molar concentration of CO_2 dimers on the distance along the axis of the jet in calibers for expansion of pure gas from a chamber with $D = 150 \mu\text{m}$, $T_0 = 300^\circ\text{K}$, and $p_0 = 10^5 \text{ Pa}$. We see that the concentration \bar{x}_2 is reached at approximately $z/D \approx 2.5$. As shown in Fig. 3, the calculated dependence (curves 1 and 2) on chamber pressure is in satisfactory agreement with the experimental dependence for the value $P = 30$. One can hardly confer a physical interpretation to this particular value of P . The fact that the parameter P is larger than unity is mainly due to the incompleteness of the model, in which the inaccuracy in the assumed functional form of the constants and parameters (for example $\bar{\nu}$, D_0) is effectively compensated for by the single constant P .

We note that the experimental data in [2] were obtained using a mass spectrometer with high-energy ionizing electrons ($\sim 70 \text{ eV}$). In this case one cannot rigorously identify the observed concentration of cluster ions with the concentrations of neutral CO_2 dimers and trimers. Nevertheless the concentrations of dimers calculated with the above parameters also accurately describe the results of the experiment [4], in which the energy of the electrons was lower ($\sim 30 \text{ eV}$). Evidently the fragmentation of larger associations by electron collision were insignificant in the experiments [2, 4], since the content of associations in the jet decreases sharply with their size. Indeed, as shown in [20], which was devoted to IR-spectroscopy of N_2O dimers in a molecular beam, at fairly low chamber pressures the

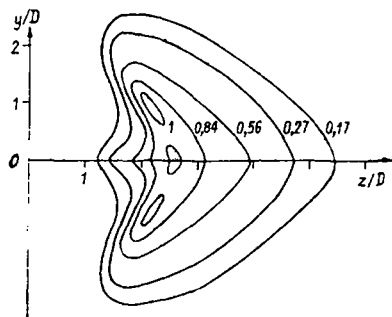


Fig. 5

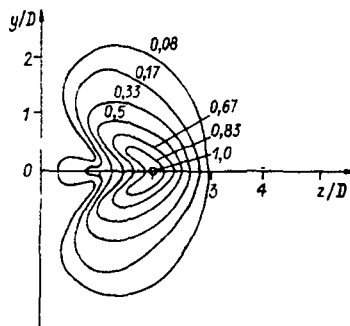


Fig. 6

mass spectrum corresponds to the actual content of neutral dimers and trimers almost independently of the energy of the electrons. For our purposes it is important that the above choice of parameters (P , \bar{v} , D_0) ties the calculated concentrations to the only available experimental data on the concentration of CO_2 dimers in expanding gas jets [2, 4]. This provides a basis for the assumption that the calculated concentration field will also be close to the actual.

In addition to dimerization reactions of the type (1.1), we also took into account processes limiting dimerization at high pressures. As a process of this kind we took the additional reaction



which was switched on at the point where the translational temperature reached 50°K . The rate constant of the reaction (3.3) was set equal to $K_3 = 1.8 \cdot 10^{11} \text{ T}^{1/2} \text{ cm}^3/(\text{sec} \cdot \text{mole})$, in correspondence with [21]. As shown in Fig. 4, this choice of K_3 and the point where the reaction switched on gives good agreement between the calculated concentrations of trimers and the mass spectrometry data [21] (the notation is analogous to that of Fig. 3).

The simultaneous solution of (1.7) and the kinetic equation for the reaction (3.3) was carried out for two cases. In the first case it was assumed that dimerization proceeds upon expansion of pure CO_2 from an axisymmetric aperture of diameter $D = 150 \mu\text{m}$ from a chamber with $T_0 = 300^\circ\text{K}$ and $p_0 = 10^5 \text{ Pa}$. The results are shown in Fig. 5 in the form of lines of equal volumetric concentration of dimers $n_2 = N_2/V = \text{const}$, where the central level corresponds to $n_2 = 9 \cdot 10^{15} \text{ cm}^{-3}$ and relative values are given for the other levels. It is evident that the surface of maximum concentration of dimers has the shape of a cone whose vertex lies at $z/D \approx 2.5$ and the angle at the vertex is of order 120° . In the cross section passing through the vertex of the cone the concentration of dimers falls off by a factor of five at a distance of two calibers from the axis of the jet.

In the second case the flow of a mixture of 95% (by weight) Ar and 5% CO_2 was calculated. The chamber pressure was set equal to 10^6 Pa and T_0 and D were taken to be the same values as in the first case. The results are shown in Fig. 6. Here the vertex of the cone of maximum concentration is located at $z/D \approx 2$ and the angle at the vertex is about 80° . The maximum value of n_2 at the central level is $1.4 \cdot 10^{17} \text{ cm}^{-3}$.

It is interesting to note that the CARS spectra of CO_2 dimers were obtained in [13] at $z/D \approx 2$ for expansion of a mixture of 95% He and 5% CO_2 into a vacuum from a chamber with $p_0 = (9-18) \cdot 10^5 \text{ Pa}$. Besides the monomer and dimer bands, wide bands were observed in [13] at $\nu = 1275.3$ and 1281.3 cm^{-1} , corresponding to CO_2 polymers and trimers, respectively. The intensities of these bands were larger than that of the dimer band. However, according to the estimates given here, the concentration of dimers exceeds that of trimers by at least an order of magnitude for the conditions of the experiment [13]. Comparison of these results provides indirect evidence to support the assumption that the cross section for Raman scattering of CO_2 trimers is significantly larger than the cross section for scattering of dimers. Unfortunately, there is practically no information in the literature on the ratio of Raman scattering cross sections of dimers and trimers. The only work is [22], in which the Raman spectra of the dimers and trimers $(\text{HCN})_2$ and $(\text{HCN})_3$ was studied. It was shown that for these associations of triatomic linear molecules the Raman cross section of the trimer band ν_1 was about 6.5 times larger than the Raman cross section of the dimer.

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