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Chemical Physics Letters 377 (2003) 663–671
CHEMICAL PHYSICS LETTERS
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Non-equilibrium dissociation rates in expanding flows

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Received 25 April 2003; in final form 11 July 2003

Abstract

In this Letter, non-equilibrium dissociation rates in expanding gas flows are studied taking into account state-to-state vibrational–chemical kinetics. A comparison of the results obtained in the state-to-state approach with the ones based on the quasi-stationary two-temperature vibrational distributions for harmonic and anharmonic oscillators and on the thermal equilibrium one-temperature distribution is presented. The influence of vibrational energy transition probabilities and nozzle profiles on vibrational level populations and dissociation rates is also discussed.
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1. Introduction

Investigation of non-equilibrium reacting gas mixture flows requires experimental data and theoretical models for reaction rate coefficients. Experiments carried out in high temperature and high enthalpy flows show noticeable deviations of reaction rates from the Arrhenius law. Since experimental data obtained under strongly non-equilibrium conditions are limited, adequate theoretical models for the reaction rates taking into account non-equilibrium vibrational distributions should be elaborated. Originally non-equilibrium contributions to reaction rates have been studied for a spatially homogeneous gas, and then for various gas flows. Several approaches for calculation of non-equilibrium dissociation rates have been developed using different molecular distributions over velocities and internal energies. One-temperature models use distributions deviating weakly from the thermal equilibrium one-temperature Maxwell–Boltzmann distribution [1,2]. A two-temperature approach is based on the quasi-stationary non-equilibrium Boltzmann or Treanor vibrational distributions [2–6]. Under strong non-equilibrium conditions these models become not to be valid, and a more rigorous approach using state-to-state distributions for determination of the reaction rates is needed. General algorithms for the reaction rates computation taking into account non-Maxwellian state-to-state distributions are given in [14].

In the recent years some authors calculated the reaction rates on the basis of state-to-state dis-

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0009-2614/$ - see front matter © 2003 Published by Elsevier B.V.
doi:10.1016/S0009-2614(03)01213-2

tributions in different gas flows: in a relaxation zone behind shock waves [7–10]; in a non-equilibrium boundary layer [11,12]; and in a nozzle expansion [13]. These studies brought new interesting results, however some peculiarities of non-equilibrium reaction rates require further investigation. Thus, recent calculations [13,15,16] performed for nozzle flows demonstrate a noticeable deviation of vibrational level populations in nozzles from the equilibrium ones and also from the quasi-stationary two-temperature distributions. The aim of the present Letter is to analyze how strong non-equilibrium vibrational distributions influence the global dissociation rate in a nozzle flow and to compare dissociation rates obtained in different approaches. Besides that, two other effects are discussed in the present Letter: the influence of different vibrational energy transition probabilities and nozzle profiles on the vibrational level populations and dissociation rates in the expanding flows of O_2/O and N_2/N mixtures.

2. Dissociation rates in different approaches

We consider a dissociation–recombination reaction

$$A_2(i) + M \rightleftharpoons A + A + M, \tag{1}$$

where $A_2(i)$ is a diatomic molecule at the vibrational level i, and M is an inert partner M which could be a molecule or an atom A.

The averaged rate coefficient $k_{\mathrm{diss}}^{(\mathrm{M})}$ of reaction (1) is defined as:

$$k_{\mathrm{diss}}^{(\mathrm{M})} = \frac{1}{n_{\mathrm{mol}}} \sum_{i=0}^{L} n_i k_{i,\,\mathrm{diss}}^{(\mathrm{M})}. \tag{2}$$

Here n_i is the population of ith vibrational level, $n_{\mathrm{mol}} = \sum_{i=0}^{L} n_i$ is the total number of molecules in the unit volume, L is the number of vibrational levels of a molecule, $k_{i,\,\mathrm{diss}}^{(\mathrm{M})}(T)$ is the state-to-state dissociation rate coefficient depending on the vibrational level of a dissociating molecule. The expressions for $k_{i,\,\mathrm{diss}}^{(\mathrm{M})}(T)$ in terms of the dissociation cross-sections based on the rigorous kinetic theory are given in [14].

For the practical calculations, state dependent rate coefficients $k_{i,\,\mathrm{diss}}^{(\mathrm{M})}$ are usually connected with the thermal equilibrium rate coefficient $k_{\mathrm{diss,\,eq}}^{(\mathrm{M})}$ by the expression:

$$k_{i,\,\mathrm{diss}}^{(\mathrm{M})} = Z_i k_{\mathrm{diss,\,eq}}^{(\mathrm{M})}, \tag{3}$$

where the non-equilibrium factor Z_i can be found using, for instance, the Treanor–Marrone model [3]. The state-to-state non-equilibrium factor has been obtained in [8,18] in the form:

$$Z_i(T,U) = \frac{Z_{\mathrm{vibr}}(T)}{Z_{\mathrm{vibr}}(-U)} \exp\left(\frac{\varepsilon_i}{k}\left(\frac{1}{T} + \frac{1}{U}\right)\right), \tag{4}$$

where $Z_{\mathrm{vibr}}(T)$ is the vibrational partition function, ε_i is the vibrational energy of a molecule at the ith level, k is the Boltzmann constant, D is the dissociation energy, U is the parameter of the model, it has a dimension of temperature and describes how rapidly the dissociation probability decreases for low levels. The case $U = \infty$ corresponds to the equal probability of dissociation from any vibrational level. Different values of the parameter U are basically used for the calculation of dissociation rate coefficients: $U = D/6k$, $U = D/3k$, $U = 3T$. A comparison of $k_{i,\,\mathrm{diss}}^{(\mathrm{M})}$ found from expressions (3) and (4) with various values of the parameter U and by means of the rigorous quasi-classical method, is given in [19] as well as recommendations for the parameter choice.

Thermal equilibrium rate coefficient $k_{\mathrm{diss,\,eq}}^{(\mathrm{M})}$ is usually expressed by the generalized Arrhenius law:

$$k_{\mathrm{diss,\,eq}}^{(\mathrm{M})} = AT^n \exp\left(-\frac{D}{kT}\right). \tag{5}$$

In the present Letter values A and n are taken from [20]; for N_2: $n = -1.6$, $A = 3.7 \times 10^{15}$ if partner M is a molecule, $A = 1.6 \times 10^{16}$ if M is an atom; for O_2: $n = -1.5$, $A = 1.99 \times 10^{15}$ and $A = 9.99 \times 10^{15}$ for the cases when M stands for a molecule and for an atom, respectively. The dimension of rate coefficients is m^3/s mol.

It is seen from Eq. (2) that the averaged dissociation rate coefficient is determined by non-equilibrium level populations. In the present Letter coefficients $k_{\mathrm{diss}}^{(\mathrm{M})}$ have been calculated using several

models for the vibrational distributions. In the most rigorous state-to-state approach, level populations and the gas temperature are found as a numerical solution of $L+1$ equations of detailed vibrational–chemical kinetics for n_i and n_{at} coupled with gas dynamic equations for the temperature and velocity. These equations for the case of a steady-state quasi-one-dimensional inviscid nozzle flow of a binary mixture A_2/A with VV, VT vibrational energy transitions, dissociation and recombination are reported in [16,17].

More simple but less accurate models are based on quasi-stationary vibrational distributions. The Boltzmann distribution with vibrational temperature $T_{\mathrm{v}} \neq T$ is valid in a system of molecules – harmonic oscillators. The Treanor distribution establishes in a system of anharmonic oscillators due to the non-resonant VV′ exchange [21]:

$$n_i = \frac{n_{\mathrm{mol}}}{Z_{\mathrm{vibr}}(T, T_1)} \exp\left(-\frac{\varepsilon_i - \mathrm{i}\varepsilon_1}{kT} - \frac{\mathrm{i}\varepsilon_1}{kT_1}\right), \tag{6}$$

here T_1 is the temperature of the first vibrational level,

$$Z_{\mathrm{vibr}}(T, T_1) = \sum_{i=0}^{L} \exp\left(-\frac{\varepsilon_i - \mathrm{i}\varepsilon_1}{kT} - \frac{\mathrm{i}\varepsilon_1}{kT_1}\right). \tag{7}$$

Distribution (6) coincides with the non-equilibrium Boltzmann distribution with $T_{\mathrm{v}} = T_1 \neq T$ if the vibrational energy ε_i is simulated by the harmonic oscillator model.

The Treanor distribution describes correctly vibrational kinetics only in the case of moderate vibrational excitation or at $T_1 < T$. Under conditions of strong vibrational excitation, various mechanisms of vibrational relaxation dominate at different groups of vibrational levels [22]. Thus, at low levels non-resonant VV′ transitions are the most probable ones, at the intermediate levels near-resonant VV″ exchanges between the neighboring states dominate, and at high levels probabilities of all vibrational energy transitions become comparable. It leads to different relations between relaxation times along the vibrational spectrum. In this case, the vibrational distribution has different forms at various groups of vibrational levels [17,23]:

$$n_i = \begin{cases} \frac{N_1}{Z^{v1}} \exp\left(-\frac{\varepsilon_i - \mathrm{i}\varepsilon_1}{kT} - \frac{\mathrm{i}\varepsilon_1}{kT_1}\right), & 0 \leqslant i \leqslant i_*, \\ n_{\mathrm{mol}} \frac{\Gamma}{i+1}, & i_* \leqslant i \leqslant i_{**}, \\ \frac{N_3}{Z^{v3}} \exp\left(\frac{\varepsilon_i}{kT}\right), & i_{**} \leqslant i \leqslant L. \end{cases} \tag{8}$$

Level i_* corresponds to the minimum of the Treanor distribution, level i_{**} is defined from the ratio of probabilities of VV and VT transitions [22]. Parameters N_1, N_3 and Γ can be defined in terms of T, T_1 and n_{mol} from the normalizing conditions and continuity of distribution at $i = i_*$, $i = i_{**}$; Z^{v1} Z^{v3} are the partition functions:

$$Z^{v1} = \sum_{i=0}^{i_*} \exp\left(-\frac{\varepsilon_i - \mathrm{i}\varepsilon_1}{kT} - \frac{\mathrm{i}\varepsilon_1}{kT_1}\right), \tag{9}$$

$$Z^{v3} = \sum_{i=i_{**}}^{L} \exp\left(-\frac{\varepsilon_i}{kT}\right). \tag{10}$$

Distribution (8) represents the Treanor distribution at low levels, a declining plateau at the intermediate levels and the Boltzmann distribution at high levels. It has been obtained first in [22] as an approximate solution of balance equations for vibrational level populations in a pure gas, and then, it has been derived from the kinetic theory principles in [23]. In [17] the model has been extended for a dissociating gas.

Using the analytical distributions, the system of macroscopic equations can be significantly simplified [6,17]. In a binary mixture A_2/A, $L+1$ equations for the vibrational level populations are reduced to the equation of two-temperature chemical kinetics for the molecular number density n_{mol}, and relaxation equation for the vibrational temperature T_{v} (harmonic oscillators) or T_1 (anharmonic oscillators). These two equations are coupled to the conservation equations of momentum and energy. The two-temperature dissociation rate coefficients $k_{\mathrm{diss}}^{(M)}(T, T_{\mathrm{v}})$ or $k_{\mathrm{diss}}^{(\mathrm{M})}(T, T_1)$ based on quasi-stationary distributions are easily derived substituting corresponding distributions to the definition (2).

Under thermal equilibrium conditions, when all internal energy exchanges proceed much faster than chemical reactions, vibrational level populations are described by the equilibrium Boltzmann distribution with the gas temperature $T = T_{\mathrm{v}}$. In

this case, the system of macroscopic equations consists of two equations of one-temperature chemical kinetics for n_{mol} and n_{at}, and conservation equations for energy and momentum. The dissociation rate coefficient is determined only by the gas temperature and satisfies to the Arrhenius formula (5), i.e., $k_{\mathrm{diss}}^{(\mathrm{M})}(T) = k_{\mathrm{diss,eq}}^{(\mathrm{M})}$.

3. Results

Nozzle flows of O_2/O and N_2/N mixtures have been studied using the state-to-state and three quasi-stationary models based on the two-temperature distribution (8), non-equilibrium Boltzmann distribution ($T_{\mathrm{v}} \neq T$) and thermal

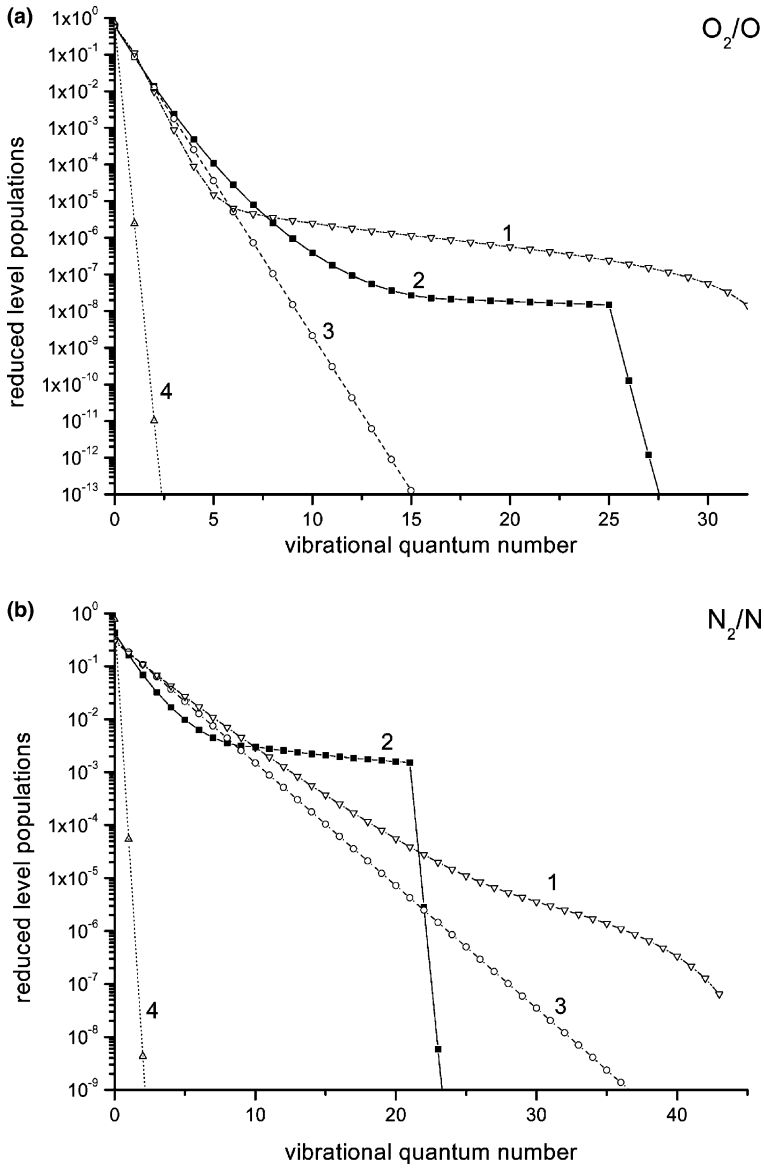

Fig. 1. Reduced level populations n_i/n versus i at $x/R = 50$ in a conic nozzle. (a) O_2/O, $T_* = 4000$ K, $p_* = 1$ atm; (b) N_2/N, $T_* = 7000$ K, $p_* = 1$ atm. Curves 1: state-to-state model; 2: two-temperature anharmonic oscillator model; 3: two-temperature harmonic oscillator model and 4: one-temperature model.

equilibrium Boltzmann distribution. The following conditions in the throat are considered: for O_2/O mixture, $T_* = 4000$ K, $p_* = 1$ atm; for N_2/N mixture, $T_* = 7000$ K, $p_* = 1$ atm. Systems of flow equations in the state-to-state and three quasi-stationary approaches have been solved numerically in [16,17], and the evolution of level populations and macroscopic parameters along the nozzle axis has been found. State-to-state distributions are obtained as a solution of the equations for level populations coupled with conservation equations whereas in the quasi-stationary approaches vibrational level populations have been computed substituting the temperature values found in the corresponding approach to the analytical distributions. In the present Letter, level populations and temperatures obtained in [16,17] are used as input data for the calculation of rate

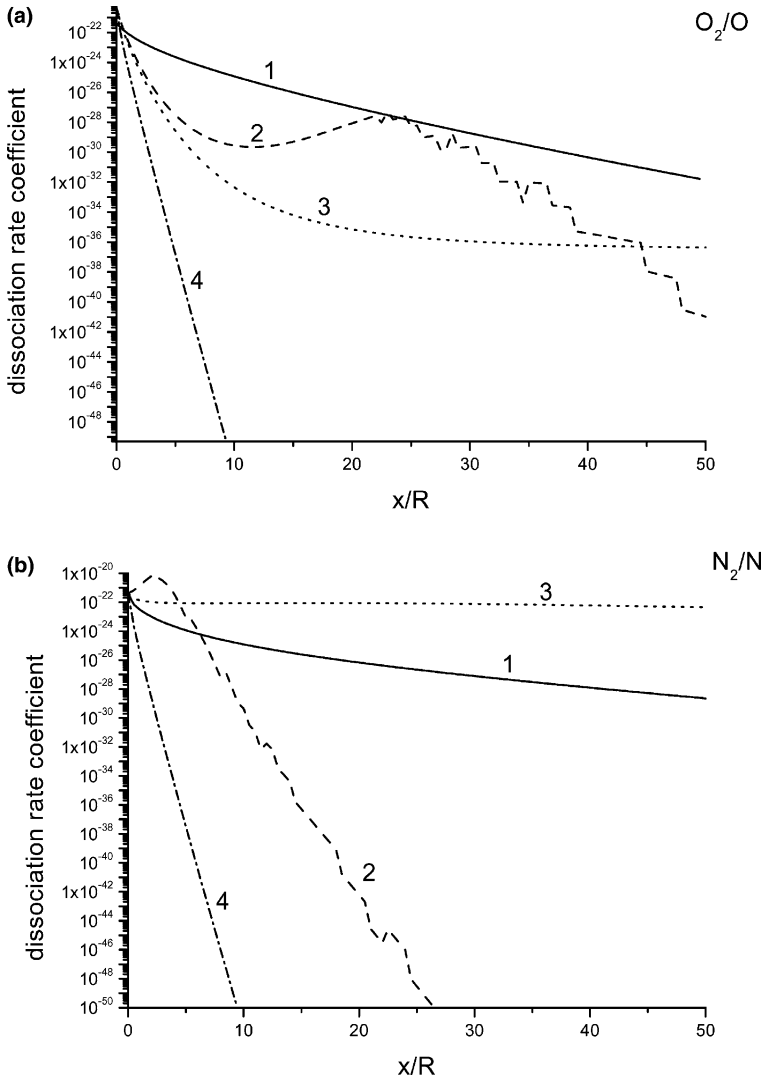

Fig. 2. Averaged dissociation rate coefficient $k_{\mathrm{dis}}^{(\mathrm{mol})}$ (m^3/s) versus x/R in a conic nozzle. (a) O_2/O, $T_* = 4000$ K, $p_* = 1$ atm; (b) N_2/N, $T_* = 7000$ K, $p_* = 1$ atm. Curves 1: state-to-state model; 2: two-temperature anharmonic oscillator model; 3: two-temperature harmonic oscillator model and 4: one-temperature model.

coefficients of dissociation at collisions with a molecule A_2 or an atom A, $k_{\mathrm{diss}}^{(\mathrm{mol})}$ and $k_{\mathrm{diss}}^{(\mathrm{at})}$. Three nozzle profiles are studied:

1. the axis-symmetric conic nozzle with a semi-angle 21° and throat radius $R = 1$ mm;
2. the nozzle studied in [24] with the profile of the divergent part:

$$\frac{S(x)}{S(x_*)} = 1 + x^2 \left(\frac{\tan\theta}{x_*} \right)^2, \tag{11}$$

where S is the section area and x_* is the throat location;

3. F4 nozzle [13]:

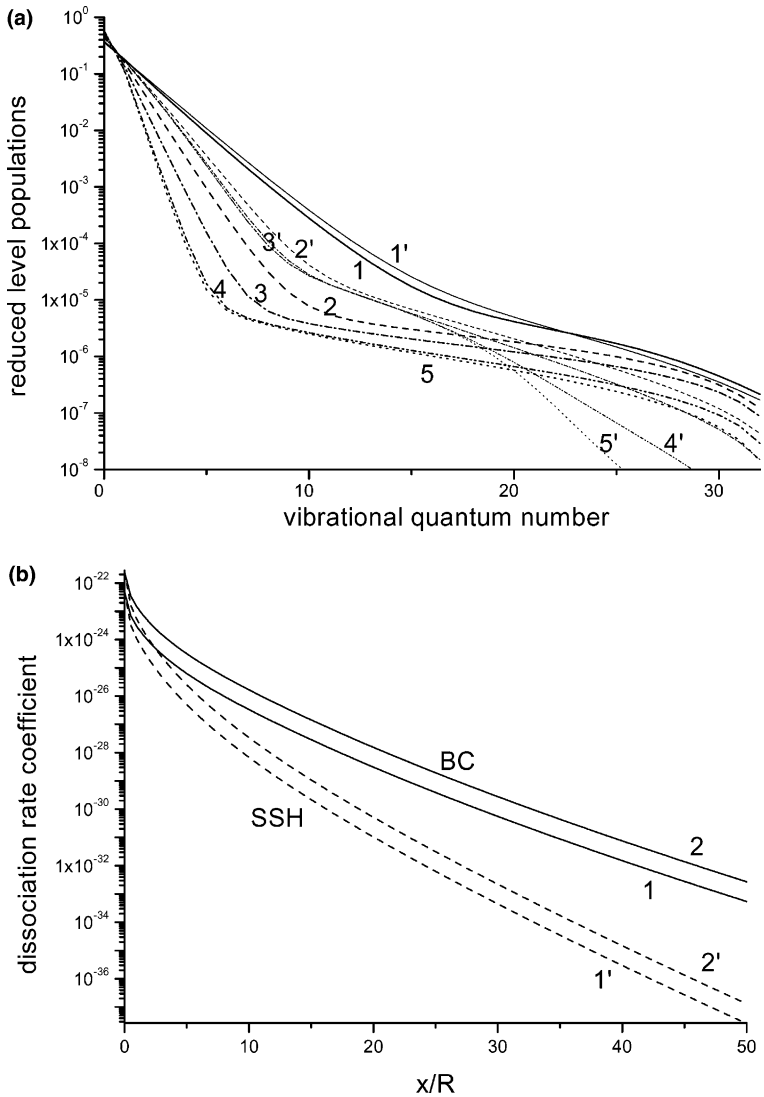

Fig. 3. The influence of VV and VT transition probabilities. O_2/O, $T_* = 4000$ K, $p_* = 1$ atm, conic nozzle. Solid lines: BC model, dashed lines: SSH model. (a) Reduced level populations n_i/n versus i at different x/R. Curves 1–5 (1′–5′) correspond to $x/R = 1,\ 5,\ 10,\ 30,\ 50$. (b) Averaged dissociation rate coefficients (m^3/s) versus x/R. Curves $1, 1'$: $k_{\mathrm{dis}}^{(\mathrm{mol})}$, curves $2, 2'$: $k_{\mathrm{dis}}^{(\mathrm{at})}$.

$$r(x) = 0.0959 - 0.0908\exp(-4.9204(x-0.5)^2),$$
$$x < 0.5m$$
$$r(x) = 0.3599 - 0.2277\exp(-0.1884(x-0.5)^2) - \frac{0.0184}{(x-0.5)^2 + 0.1447}, \quad x \geqslant 0.5m \tag{12}$$

In the state-to-state approach, rate coefficients for VV, VT vibrational energy transitions are required for the production terms calculation. Two models for VV and VT transitions are considered in this study: the model reported in paper [12] where the interpolating formulas for rate coefficients obtained by means of molecular dynamics methods [25,26] are proposed (hereafter this model is referred to as the BC-model), and the SSH

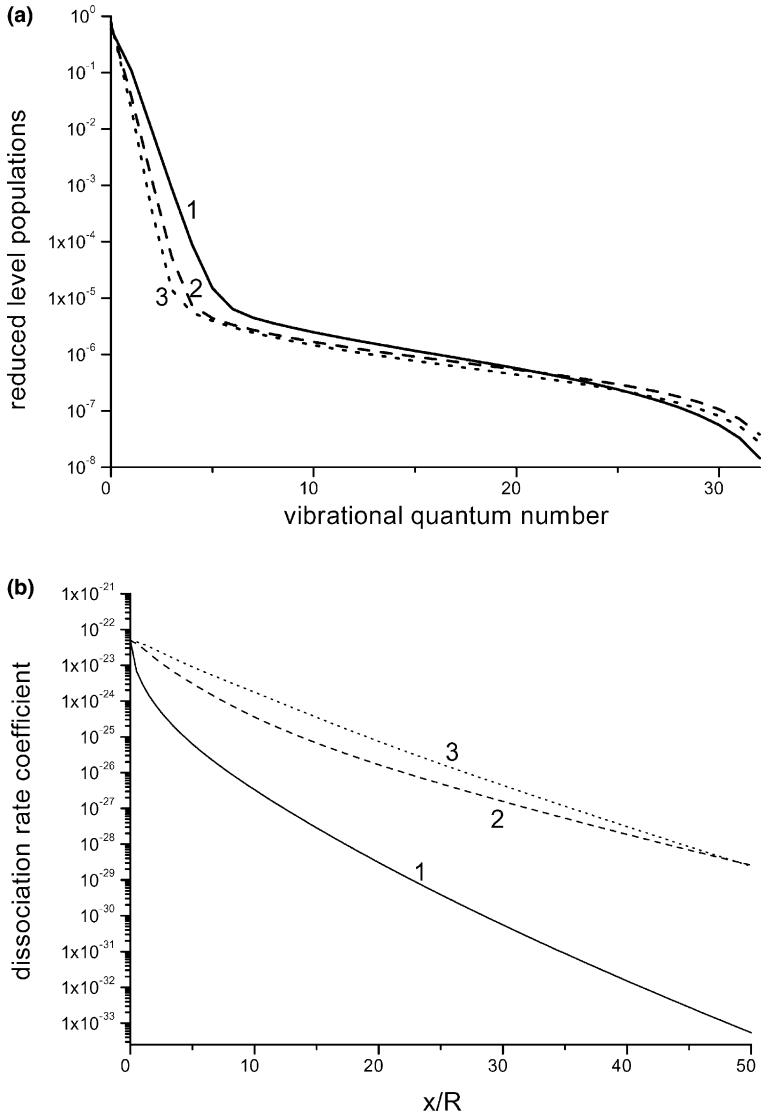

Fig. 4. The influence of a nozzle profile. O_2/O, $T_* = 4000$ K, $p_* = 1$ atm, conic nozzle. Curve 1: conic nozzle; 2: nozzle (11); 3: nozzle F4 (12). (a) Reduced level populations n_i/n versus i at $x/R = 50$. (b) Averaged dissociation rate coefficient $k_{\mathrm{dis}}^{(\mathrm{mol})}$ (m^3/s) versus x/R.

model [27] based on the first order perturbation theory. The influence of the model on the vibrational distributions and dissociation rates is also discussed below.

In Fig. 1 state-to-state distributions are compared with the ones calculated using the quasi-stationary approximations at $x/R = 50$, x is the distance from the throat and R is the throat radius. Curves (1) plot state-to-state distributions, curves (2) correspond to complex distributions (8) for anharmonic oscillators, curves (3) depict non-equilibrium Boltzmann distributions for harmonic oscillators and curves (4) show one-temperature thermal equilibrium distributions. A significant distinction between the distributions growing with increasing the distance from the the throat can be noticed. Thermal equilibrium distributions give an essential underestimation of populations of all levels. For low levels, quasi-stationary models for both harmonic and anharmonic oscillators lead to populations close to the ones obtained by means of the state-to-state approach while for other levels the difference between distributions provided by various models is rather high.

The averaged dissociation rate coefficient $k_{\mathrm{diss}}^{(\mathrm{mol})}$ calculated in four approaches using distributions discussed above, is presented in Fig. 2. One can see a quite strong influence of the kinetic model on the averaged dissociation rate coefficients, all quasi-stationary models give the values of $k_{\mathrm{diss}}^{(\mathrm{mol})}$ rather far from the ones obtained in the rigorous state-to-state approximation, the same effect is obtained for $k_{\mathrm{diss}}^{(\mathrm{at})}$. In all considered cases, $k_{\mathrm{diss}}^{(\mathrm{at})}$ is higher than $k_{\mathrm{diss}}^{(\mathrm{mol})}$, i.e., atoms are more efficient as partners in the dissociation process. It is interesting to note that, as it was shown in [16], the difference between macroscopic parameters and transport properties in nozzles calculated using the state-to-state and quasi-stationary models is not so high as for the dissociation rate coefficients. It can be explained by the fact that the gas temperature and transport properties are mainly determined by the populations of several low vibrational states, where distributions in all approximations are not so far one from another. On the contrary, a significant contribution to dissociation rate coefficients comes from the high vibrational states where distributions, found in various approaches differ considerably. A strong influence of vibrational distributions on non-equilibrium dissociation rates has been found also in flows behind shock waves [18].

Another important aspect is the effect of VV and VT transition probabilities on vibrational distributions and dissociation rates. Vibrational level populations and averaged dissociation rate coefficients $k_{\mathrm{diss}}^{(\mathrm{mol})}$, $k_{\mathrm{diss}}^{(\mathrm{at})}$ calculated in the state-to-state approach using the SSH and BC model are given in Fig. 3. One can see a considerable discrepancy between the results obtained on the basis of two models for VV and VT transition rates. The SSH model underestimates noticeably the vibrational distributions as well as the dissociation rate in a nozzle flow.

Finally, the influence of a nozzle profile on state-to-state distributions and dissociation rates has been studied. The results are presented in Fig. 4. A behaviour of vibrational distributions appears to be similar in all cases, a small difference is obtained only for a conic nozzle. However, this difference results in a significant discrepancy between the averaged dissociation rate coefficients. Thus the rate of dissociation is found to be considerably lower in a conic nozzle compared to nozzles (11) and (12).

4. Conclusions

The vibration–chemical kinetics and dissociation rate coefficients in various nozzle flows have been studied using four kinetic theory approaches: the detailed state-to-state model; non-equilibrium two-temperature models for anharmonic and harmonic oscillators; the thermal equilibrium one-temperature model. The influence of these approaches, vibrational transition probabilities and nozzle profile on vibrational state populations and averaged dissociation rate coefficients has been estimated. It is shown that vibrational distributions affect essentially the dissociation rate coefficients. An important impact of transition probabilities not only on the level populations but also on dissociation rates is found.

Acknowledgements

This work is partially supported by the Russian Foundation for Basic Research (project 02-03-42044).

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