

On a role of multi-level energy transitions in the state-to-state vibrational-chemical kinetics

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Abstract. In this paper the state-to-state vibration-dissociation-recombination kinetics in binary mixtures of diatomic molecules and atoms with different initial conditions is considered. The influence of initial mixture composition and vibrational non-equilibrium on level populations, macroscopic parameters and relaxation time is studied. Dissociation, recombination, VV and TV vibrational energy transitions are taken into account and an important role of multi-level jumps at the molecule-atom collisions is shown. The comparison of two dissociation models and their influence on gas parameters is presented. Quite different character of relaxation processes is found for weak and strong initial vibrational non-equilibrium.

Keywords: Non-equilibrium vibrational-chemical kinetics, Dissociation, State-to-state kinetics, Multi-level vibrational transitions.

PACS: 51.10.+y

INTRODUCTION

In recent years serious progress has been reached in creation of accurate models of vibrational-chemical kinetics in different gas flows (see references in the books [1, 2]). However, there remain some aspects of this problem, which are studied not sufficiently up to now and should be considered in order to improve the accuracy of mathematical models of non-equilibrium kinetics.

One of such effects concerns a role of multi-level vibrational energy jumps in relaxation processes. Most often these transitions are neglected in solving the equations of state-to-state kinetics and only one-level jumps are considered. Multi-level transitions have been taken into account only in some papers [3]. However, the influence of multi-level transitions on vibrational distributions and macroscopic gas parameters has not been evaluated up to now.

In the present paper the effect of multi-level jumps is studied numerically for a wide range of temperatures in non-stationary mixtures (N_2 , N). Equations for state-to-state vibration-dissociation-recombination kinetics coupled to the equations for the gas temperature and atomic densities are solved for different initial conditions for distributions and mixture composition. Anharmonic molecular vibrations with one-quantum and multi-quantum transitions are taken into account. Dissociation has been described with use the Treanor-Marrone model [4] and ladder-climbing one [3]. Effects of multi-level jumps, initial non-equilibrium and mixture composition in relaxation processes, as well as a role of anharmonicity of vibrations and a model of elementary processes are investigated.

THEORETICAL MODEL

We consider state-to-state kinetics in space-homogeneous binary mixtures of molecules A_2 and atoms A with various initial distributions and mixture composition, taking into account dissociation - recombination



and VV and VT vibrational energy transitions



Here i , k and i' , k' are vibrational levels numbers, M is a partner which can be a molecule or an atom.

On the basis of experimental data for vibrational and rotational relaxation times, distributions over rotational levels are supposed to be equilibrium and VR and VRT energy transitions are neglected. The time evolution of vibrational

level populations $n_i(t)$, number density of atoms $n_{at}(t)$ and gas temperature $T(t)$ satisfy the following equations

$$\frac{dn_i}{dt} = R_i^{VV} + R_i^{VT} + R_i^{dis-rec}, \quad i = 1, 2 \dots L. \quad (4)$$

$$\frac{dn_{at}}{dt} = R_a. \quad (5)$$

$$\frac{3}{2}(n_{at} + n_{mol})kT + n_{mol}kT + \sum_{i=0}^L \varepsilon_i n_i(t) = const, \quad (6)$$

here $n_{mol} = \sum_{i=0}^L n_i$, k is the Boltzmann constant, ε_i is the vibrational energy of a molecule at i -th level, i is the numbers of exited levels of the molecule A_2 .

The right-hand parts of Eqs. (4), (5) describe energy transitions (2), (3) and reactions (1) and have a form:

$$R_i^{VV} = \sum_{k,k',i'(i' \neq i, k' \neq k)} (k_{ii'}^{k'k} n_{i'} n_{k'} - k_{ii'}^{kk'} n_i n_k) \quad (7)$$

$$R_i^{VT} = \sum_{M=at,mol} n_M \sum_{i'(i' \neq i)} (k_{ii'}^M n_{i'} - k_{ii'}^M n_i), \quad (8)$$

$$R_i^{dis-rec} = \sum_{M=at,mol} n_M (k_{rec,i}^M n_{at}^2 - k_{i,dis}^M n_i), \quad (9)$$

$$R_a = -2 \sum_i R_i^{dis-rec}, \quad (10)$$

where $k_{ii'}^{k'k}(T)$, $k_{ii'}^M(T)$ are the rate coefficients of transitions (2), (3), $k_{i,dis}^M(T)$, $k_{rec,i}^M(T)$ are the rate coefficients of dissociation from the i -th level and recombination to the i -th level correspondingly. Vibrational spectra are simulated using the anharmonic oscillator model, the energy ε_i is calculated from the zeroth level energy.

Initial level populations have been taken in the form of non-equilibrium Boltzmann distribution with the vibrational temperature T_{V0} different from the initial gas temperature T_0 :

$$n_i(0) = n_{mol}(0) Z_{vibr}^{-1} \exp\left(-\frac{\varepsilon_i}{kT_{V0}}\right), \quad Z_{vibr} = \sum_i \exp\left(-\frac{\varepsilon_i}{kT_{V0}}\right). \quad (11)$$

Eqs. (4)-(6) have been solved numerically for (N_2, N) mixture for different values of T_0 , T_{V0} and $n_{at}(0)$, $n_{mol}(0)$.

The results showed the influence of initial non-equilibrium and mixture composition on distributions and macroscopic parameters. One-level and multi-level TV transitions have been taken into account. The solution has been compared with data obtained neglecting multi-level jumps and a role of multi-level vibrational transitions in considered relaxation processes has been estimated. The results are presented in the next section.

RESULTS

The results have been obtained for two cases: strong initial vibrational excitation ($T_0 = 500$, $T_{V0} = 5000$) and initially heated gas ($T_0 = 5000$, $T_{V0} = 1000$); the cases $n_{at}(0) = 0$ and $n_{at}(0) \neq 0$ are considered; $n_0 = n_{mol}(0) + n_{at}(0) = 1.474 \cdot 10^{18} \text{ cm}^{-3}$.

First, we will consider vibrational relaxation through reaction (2), (3). For calculations of rate coefficients of VV and VT vibrational energy transitions the approximate expressions proposed in [3] have been used.

Fig. 1a presents distributions (divided to the total number density $n = n_{mol} + n_{at}$) at different moments of time at the initial conditions $T_0 = 500$, $T_{V0} = 5000$, $n_{at}(0) = 0.01 n_0$.

One can observe the evolution of populations (figs. 1a,c) and gas temperature (fig. 1b) in initially vibrationally excited gas: formation of strongly non-equilibrium distribution with plateau-part at the intermediate levels due to intensive VV exchange, and then, desactivation in result of VT transitions. It can be noted that obtained distributions differ drastically from ones which take place in a system of harmonic oscillators at the same initial conditions. It is known [5] that in a latter case distributions keep the Boltzmann form during a relaxation process due to resonant

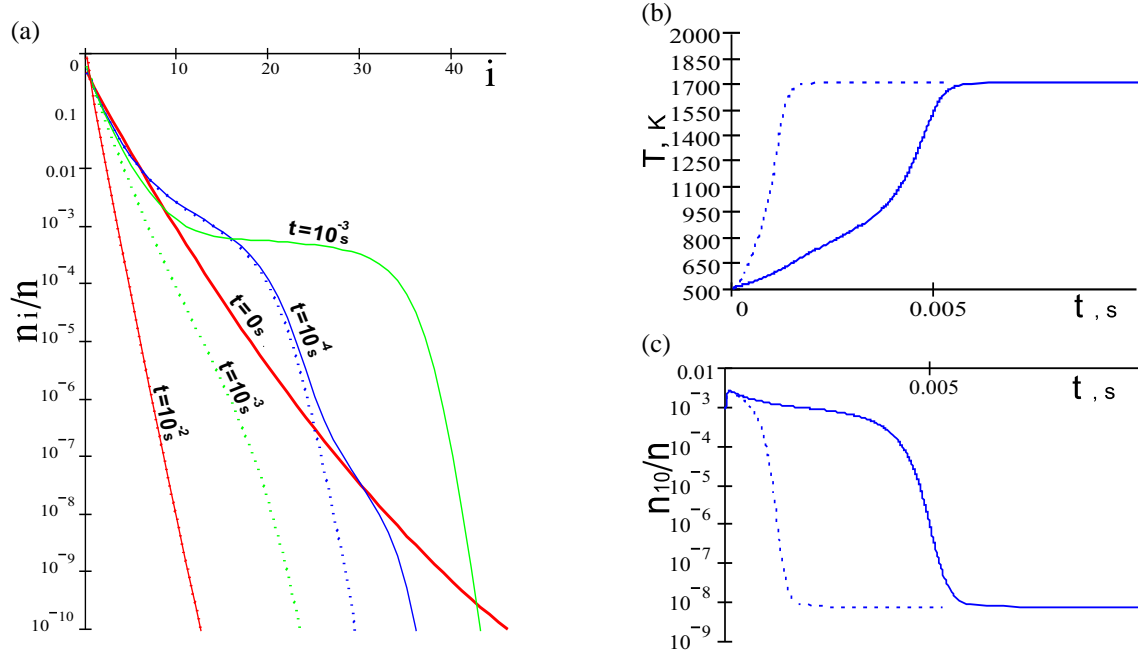


FIGURE 1. (a): n_i as a function of i . (b): gas temperature as a function of t . (c): n_{10} as a function of t . $T_0 = 500K$, $T_{V0} = 5000K$, $n_{at}(0) = 0.01n_0$. Solid lines - disregarding multi-level jumps at the molecule-atom collisions, dashed lines - with multi-level jumps.

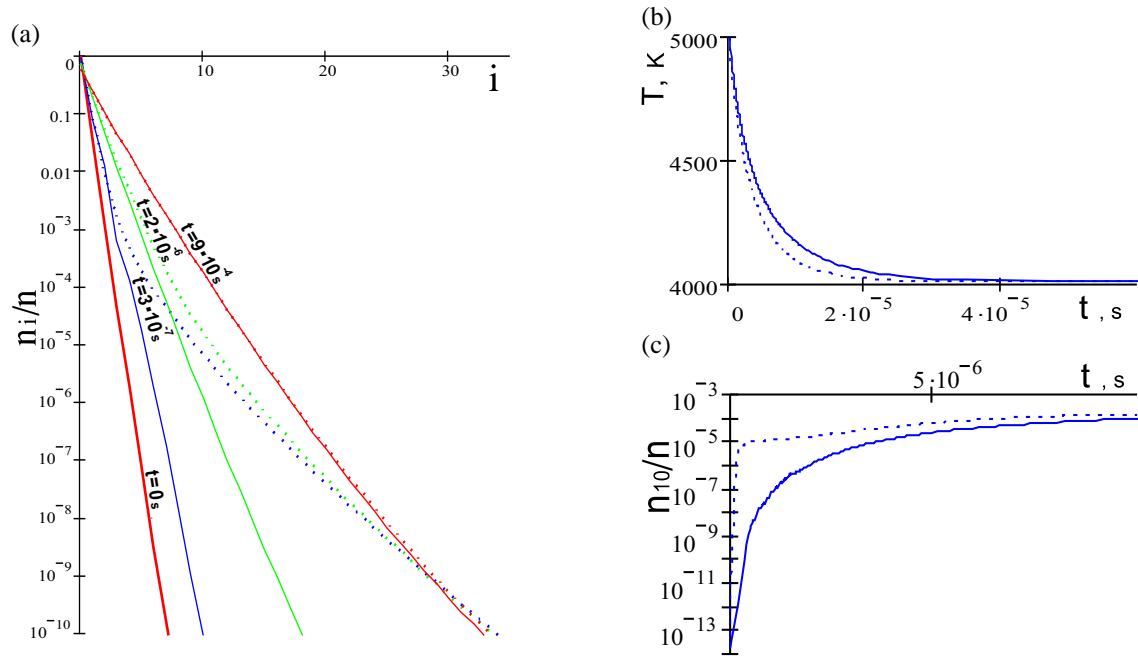


FIGURE 2. (a): n_i as a function of i . (b): gas temperature as a function of t . (c): n_{10} as a function of t . $T_0 = 5000K$, $T_{V0} = 1000K$, $n_{at}(0) = 0.01n_0$. Solid lines - disregarding multi-level jumps at the molecule-atom collisions, dashed lines - with multi-level jumps.

character of VV exchanges of harmonic oscillators. In contrast, anharmonic effects, which are particularly important in strongly excited gas, lead to deformation of initial Boltzmann distributions.

One can see that taking into account multi-levels VT^{at} transitions at the collisions of molecules with atoms (dashed lines) leads to much more rapid evolution of populations and temperature comparable to the case when only single-quantum transitions were included (solid lines). Calculations showed that at the molecule-molecule collisions the multi-level jumps play weaker role and can be neglected.

Figs. 2a,b,c report the results obtained in the case of initially heated gas: $T_0 = 5000$, $T_{V0} = 1000$, $n_{at}(0) = 0.01n_0$. It is seen that in this case the gas temperature decreases whereas populations of all levels increase smoothly with t rising. The shape of distributions is quite different comparable to the first case of strong initial vibrational excitation. Multi-quantum VT^{at} transitions are found to be significant and speed up a relaxation process however this effect is weaker than in the first case. The relaxation time appears to be much shorter in heated gas comparable to the case when $T_0 < T_{V0}$.

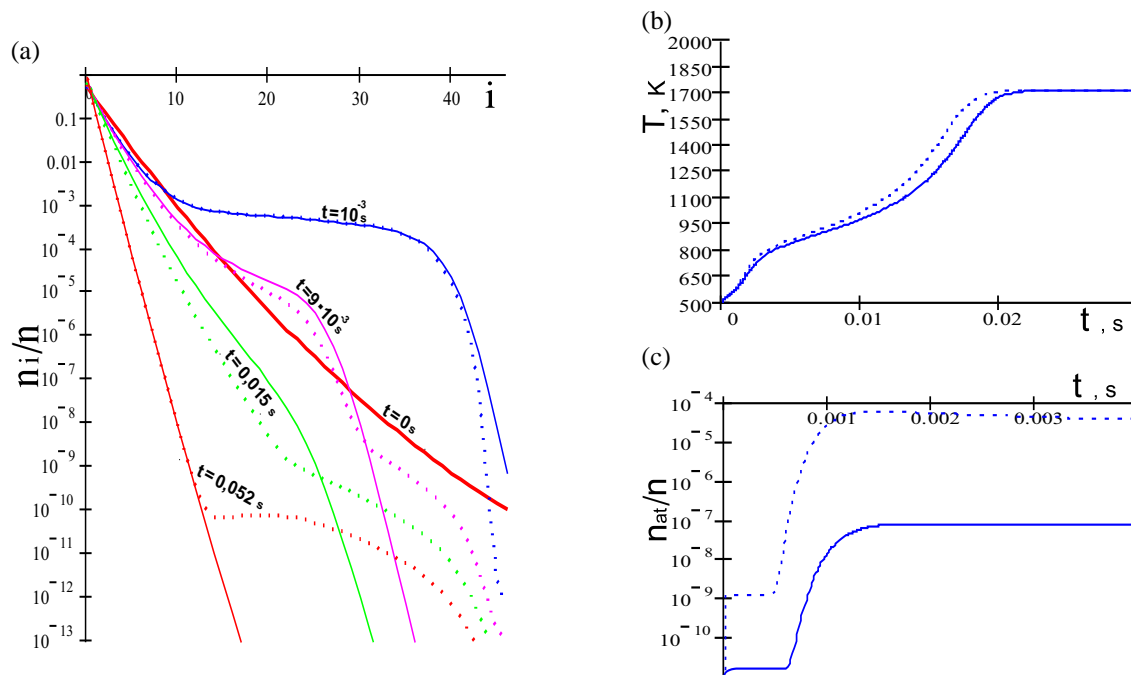


FIGURE 3. (a): n_i as a function of i . (b): gas temperature as a function of t . (c): n_{at} as a function of t . $T_0 = 500K$, $T_{V0} = 5000K$, $n_{at}(0) = 0$. Solid lines - ladder-climbing model, dashed lines - Treanor-Marrone model.

The next figs. 3, 4 depict time dependence of populations n_i , gas temperature T and number density of atoms n_{at} in (N_2, N) mixture with reactions (1), (2), (3). Dissociation was described using ladder-climbing model [3] and Treanor-Marrone model [4] generalized for the state-to-state approximation [2]. Recombination rate coefficients were calculated using detailed balance principle.

The results showed the influence of a dissociation model on vibrational distributions and macroscopic parameters. Thus, using Treanor-Marrone model, permitting dissociation from each level, leads to more intensive dissociation (increasing of $n_{at}(t)$) comparable to the ladder-climbing model when dissociation proceeds only through the last level. It should be noted that this effect manifests itself even in the case if not only single-quantum but also multi-quantum TV transitions to the last level are taken into account.

It is interesting to observe decreasing of populations of high levels due to dissociation at the first stage of a relaxation process and then, increasing of populations due to recombination of atoms appearing in result of dissociation (figs. 3a, 4a). This effect occurs more noticeable in the first case of strong vibrational excitation (fig. 3a). The results demonstrate the possibility of dissociation at low temperatures in the case of high populations of intermediate and upper vibrational levels. The influence of a dissociation model on the gas temperature is also found to be more noticeable in highly excited gas (fig. 3b) comparable to the case of heated gas (fig. 4b).

The results show that the atomic component is of considerable importance in evolution of state-to-state distributions. Increasing of initial number density of atoms leads to much more rapid relaxation processes in the considered mixture.

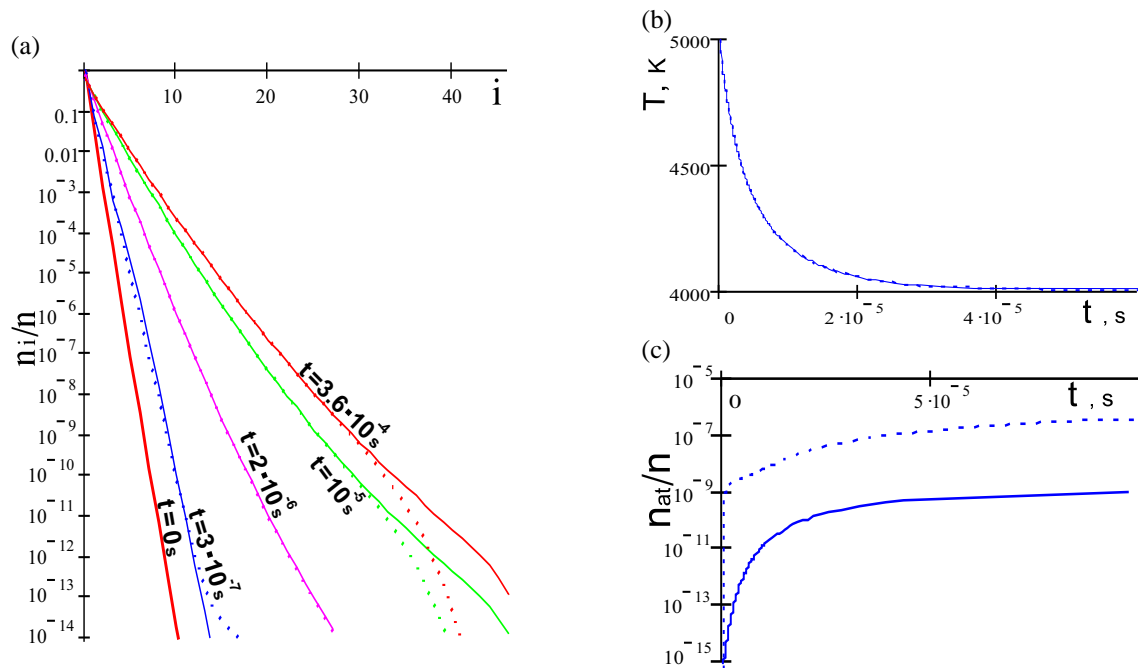


FIGURE 4. (a): n_i as a function of i . (b): gas temperature as a function of t . (c): n_{at} as a function of t . $T_0 = 5000K$, $T_{V0} = 1000K$, $n_{at}(0) = 0$. Solid lines - ladder-climbing model, dashed lines - Treanor-Marrone model.

CONCLUSIONS

Time evolution of state-to-state distributions and macroscopic parameters is studied under different initial conditions. Quite different character of vibrational-chemical relaxation is found for the cases of strong and weak non-equilibrium initial distributions. The results show that multi-level vibrational energy transitions significantly influence on vibrational distributions and macroscopic gas parameters reducing the vibration relaxation time. Neglecting of multi-quantum transitions at the collisions of molecules and atoms can lead to a considerable error in prediction of vibrational distributions and macroscopic parameters. This effect is particularly noticeable in the case of strong initial vibrational excitation ($T_0 < T_{V0}$). Comparison of ladder-climbing and Treanor-Marrone models for dissociation showed more intensive dissociation and recombination in the latter case.

The results of the paper can be used for improvement of the accuracy of mathematical models of state-to-state vibrational-chemical kinetics under different conditions.

ACKNOWLEDGMENTS

This work is supported by INTAS (project 03-51-5204).

REFERENCES

1. M. Capitelli, C. M. Ferreira, B. F. Gordiets, A. I. Osipov, *Plasma kinetics in atmospheric gases.*, Berlin: Springer-Verlag, 2000. 302p.
2. E. A. Nagnibeda, E. V. Kustova, *Kinetic theory of transport and relaxation processes in non-equilibrium reacting gas flows*, St. Petersburg Univ. Press, St. Petersburg, 2003, 270p. (in Russian).
3. M. Capitelli, I. Armenise, C. Gorse, *J. Thermophys. Heat Transfer* **11**, 4, 570-578 (1997).
4. P. Marrone, C. Treanor, *Phys. Fluids* **6**, 1215 (1963)
5. E. Montroll, K. Shuler *J. Chem. Phys.*, **26**, 454-464 (1957).