

# Time-dependent concentrations of reagents and products involved in the dissociation–recombination process

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**Abstract** The coupled vibration–dissociation–recombination process has been examined for diatomic molecules and atoms. The relationship between the concentrations of reagent molecules, product atoms and the instantaneous dissociation rate is established in an analytical form. A very accurate approach similar to the technique of uniform approximation is used to solve a relevant nonlinear differential equation. An exact analytical solution to the master equation is obtained for the model of strong collisions.

**Keywords** Master equation · Dissociation–recombination process · Reaction rate · Uniform approximation

## 1 Introduction

The time-dependent vibrational relaxation of diatomic molecules dissociating and recombining in a background of inert atoms has long been a popular topic of theoretical investigations [1–5]. Due to the progress in computer facilities and the accessibility of extensive information on realistic molecular interactions, the numerical treatments of complicated three-dimensional models of molecular collisions including dissociation–recombination events have become feasible. Nevertheless, analytical approaches provide a clear insight into the process under study, allow general conclusions, and correctly raise the problems for numerical modeling [6, 7].

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The purpose of this paper is to call attention to several aspects of the relationship between the concentrations of reagent molecules, product atoms and the instantaneous dissociation rate. A mathematical connection between these time-dependent quantities will be ascertained using the method of standard equation. The relation will be studied for the case where the simultaneous dissociation–recombination process takes place. As shown below, the time-dependent reaction rate is also given in terms of the instantaneous dissociation rate as a simple analytical formula. When one of these quantities is determined experimentally, the theory developed makes it possible to find the others from simple relationships.

In the present derivation, the molecules are assumed to distribute in a heat bath, consisting of chemically inert gas whose concentration is much higher than that of the molecules. In this case, the collisions of the molecule–molecule type may be neglected. The molecules will decompose due to collisions with inert atoms occurring at high temperatures. However, owing to the low concentration of molecules, the inert gas temperature  $T$  is kept constant with a fair accuracy. The reactant molecules are initially in the vibrational Boltzmann distribution at temperature  $T_i$  such that  $T_i < T$ . We also assume a thermal equilibrium for the translational and rotational degrees of freedom at  $T$ .

## 2 Dissociation–recombination process

Consider now the reversible chemical reaction  $M + X \rightleftharpoons 2A + X$ , where molecule  $M$  decomposes into two atoms  $A$  in a large excess of inert gas  $X$ . Further, the species  $A$  and  $X$  are taken as the structureless particles. Collisions between  $M$  and  $X$  result in a fraction  $M_n(t)$  of excited molecules at the vibrational level  $n$  at time  $t$ . These populations may be found from the master equation [1–8]:

$$\frac{d}{dt}M_n(t) = \sum_{n'} [k_{n' \rightarrow n}M_{n'}(t) - k_{n \rightarrow n'}M_n(t)] - k_{n \rightarrow c}M_n(t) + k_{c \rightarrow n}A(t)^2 \quad (1)$$

and

$$\frac{dM}{dt} = -k_d(t)M(t) + k_r A(t)^2 = -\frac{1}{2} \frac{dA}{dt}, \quad (2)$$

where the instantaneous dissociation rate is

$$k_d(t) = \sum_n k_{n \rightarrow c} \frac{M_n(t)}{M(t)} \quad (3)$$

The rotationally averaged rate coefficients for the level-to-level transitions are denoted by  $k_{n \rightarrow n'}$ , and  $c$  designates the continuum. Here  $k_r$  is the sum of all the state-specific recombination rate coefficients. All the rate coefficients are proportional to the concentration of the inert gas  $X$  and depend on its temperature  $T$ . Hereinafter,  $M(t)$  designates the concentration of molecules (the sum of all populations) and  $A(t)$  is the concentration of atoms. Since the total number of atoms is conserved, the conservation equation is taking place. Therefore, Eq. (2) leads to the conservation law

$$M(t) + \frac{A(t)}{2} = M(0) \quad (4)$$

Equation (2) may be rewritten to ascertain a useful relation between the reaction rate  $K(t)$  and the instantaneous dissociation rate

$$K(t) = -\frac{1}{M(t)} \frac{dM}{dt} = k_d(t) - k_r \frac{A(t)^2}{M(t)} \quad (5)$$

Below we are concerned with the time-dependent concentrations of the molecules and reaction products. As follows, the concentrations depend on the internal-state populations, found from Eqs. (1) and (2). We consider these problems separately. To study a qualitative character of solution to nonlinear equation (2), the level populations are assumed to be known as the time-dependent functions. In particular, the concentration of atoms may be determined from this equation. In other words, our goal is to express  $A(t)$  in terms of the instantaneous dissociation rate.

First of all, we use Eq. (4) to get the equation for the concentration of  $A$

$$\frac{dA}{dt} = -2k_r A(t)^2 - k_d(t)A(t) + 2k_d(t)M(0) \quad (6)$$

We have the nonlinear, differential equation with the time-dependent coefficients. For nonlinear problems, the generally applicable method is to solve the equation numerically. This method provides expendable solutions for one-time application that are hard to generalize. The perturbation method is useful in a limited set of situations where we first solve a linear problem and then search for nonlinear corrections. Here we offer an analytical approach which amounts to the method of standard equation [9]. The basic concept of the method is to obtain an approximate solution to the differential equation via the available exact solution to a simpler equation.

A feasible solution to the problem is quite possible if we consider the equation with constant coefficients, which we call the “standard equation”

$$\frac{dA_s}{dt} = -2\kappa_r A_s(t)^2 - \kappa_d A_s(t) + 2\kappa_d M(0) \quad (7)$$

Here, subscript “s” denotes the solution to the standard equation. The dissociation–recombination process is usually interpreted in the framework of this phenomenological rate equation [1–6]. Remember that the observed rate coefficients  $\kappa_r$  and  $\kappa_d$  are proportional to the concentration of the third inert bodies for the reaction occurring in an excess of inert gas. The nonlinear, differential equation with constant coefficients may be solved by separation of variables. Taking into account the initial condition  $A_s(0) = 0$ , we find

$$t = \int_0^{A_s} \frac{dA}{-2\kappa_r A^2 - \kappa_d A + 2\kappa_d M(0)} \quad (8)$$

The inverse of curve  $t = t(A_s)$  results in

$$A_s(t) = \frac{4M(0)}{1 + \xi_s \coth(\xi_s \kappa_d t/2)}, \quad (9)$$

where

$$\xi_s = \left(1 + \frac{16M(0)\kappa_r}{\kappa_d}\right)^{\frac{1}{2}} \quad (10)$$

Taking into account the conservation law, we obtain the concentration of the molecules

$$M_s(t) = M(0) \frac{\xi_s \coth(\xi_s \kappa_d t/2) - 1}{\xi_s \coth(\xi_s \kappa_d t/2) + 1} \quad (11)$$

Now we are in a position to find the solution to Eq. (6). Let  $k_d(t)$  be a slowly varying function of time. By virtue of Eq. (9), solution to the input equation is of the form

$$A_a(t) = \frac{4M(0)}{1 + \xi(t) \coth[y(t)]}, \quad (12)$$

where subscript “a” is applied to the approximate solution. This expression, incorporated in Eq. (6), indicates that

$$\xi(t) = \left(1 + \frac{16M(0)k_r}{k_d(t)}\right)^{\frac{1}{2}} \quad (13)$$

and  $y(t)$  is a “mapping function”

$$y(t) = \frac{1}{2} \int_0^t \xi(t') k_d(t') dt' \quad (14)$$

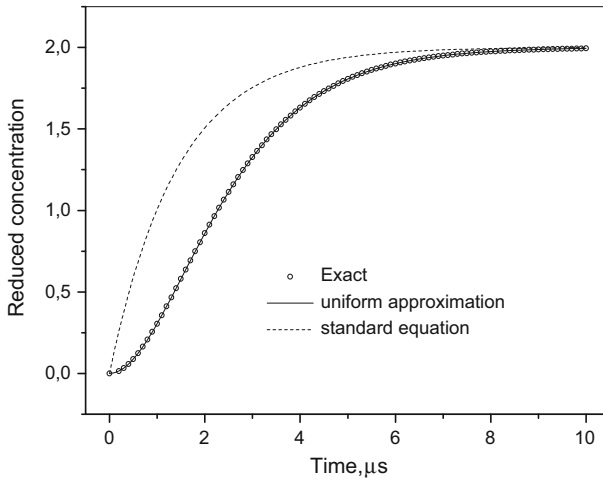
Let us discuss now the condition under which the resulting solution may be applied. To this end, we differentiate  $A_a(t)$  with respect to time and compare the result with Eq. (6). Immediately we get

$$\frac{dA_a}{dt} = -2k_r A_a(t)^2 - k_d(t) A_a(t) + 2k_d(t) M(0) + z(t), \quad (15)$$

where

$$z(t) = -\frac{A_a(t)}{\xi(t)} \frac{d\xi}{dt} \left[1 - \frac{A_a(t)}{4M(0)}\right] \quad (16)$$

Thus, the “unnecessary term”  $z(t)$  arises. When  $k_d(t)$  is time-independent,  $\dot{\xi} = 0$  and the derivatives  $dA/dt$  and  $dA_a/dt$  coincide. It is safe to assume that the approximate solution is in fair agreement with the numerically exact solution, where the term  $z(t)$  gives a minor contribution to the right-hand side of Eq. (15) as compared with the



**Fig. 1** Time dependence of the reduced concentration of atoms  $A(t)/M(0)$  at  $T = 10,000$  K and  $T_i = 300$  K in the  $O_2 + Ar$  thermal dissociation reaction

leading terms. This is confirmed by numerical calculations. The expression in square brackets decreases with increasing time from unity to  $\xi(\infty)/(1 + \xi(\infty))$ , i.e., remains finite. Obviously, the quality of solution depends on the condition that the expression before square brackets should be a perturbation parameter. The absolute value of  $\dot{\xi}/\xi$  derivative increases with time, but the concentration of  $A_a(t)$  remains very low for any length of time. At long times, the concentration of atoms tends to the finite limit, but the  $\dot{\xi}/\xi$  derivative vanishes. Thus, expression (12) gives a uniform approximation for  $A(t)$  valid for the whole range of  $t$ . These considerations are illustrated by Fig. 1, which presents the concentrations of atoms  $A$  (divided by the initial concentration of molecules), calculated from Eqs. (9), and (12) and obtained by numerical integration of Eq. (6) (see Sect. 4 for details). According to numerical calculations, the significant difference between the  $A_s(t)$  and  $A(t)$  concentrations decreases with reduction in the temperature. It is noteworthy that initially, the phenomenological equation was proposed and applied successfully to moderate temperatures.

Finally, the concentration of molecules is found from Eqs. (4) and (12)

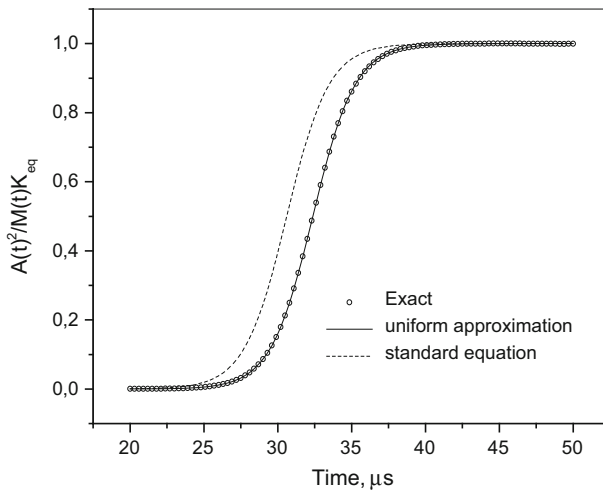
$$M_a(t) = M(0) \frac{\xi(t) \coth [y(t)] - 1}{\xi(t) \coth [y(t)] + 1} \tag{17}$$

Now we may determine the concentrations of reagents and products in the steady-state condition

$$A_a(\infty) = \frac{4M(0)}{1 + \xi(\infty)} \tag{18}$$

and

$$M_a(\infty) = M(0) \frac{\xi(\infty) - 1}{\xi(\infty) + 1} \tag{19}$$



**Fig. 2** The  $A(t)^2/M(t)K_{eq}$  ratio as a function of time at  $T = 10,000$  K and  $T_i = 300$  K

Then, the  $A_a(\infty)^2/M_a(\infty)$  ratio is equal to the ordinary rate-quotient law  $k_d(\infty)/k_r = K_{eq}$ , in which  $K_{eq}$  is the equilibrium constant of the reaction. This is a rigorous result which follows directly from Eq. (1) after substitution of the  $M_n(\infty) = \rho_n M(\infty)$  limit into this equation. A useful remark should be made on the  $k_d(\infty)$  value. It is easy to see that

$$k_d(\infty) = \sum_n k_{n \rightarrow c}(T) \frac{M_n(\infty)}{M(\infty)} = \sum_n k_{n \rightarrow c}(T) \rho_n(T), \quad (20)$$

where  $\rho_n(T)$  is the vibrational Boltzmann distribution at the heat bath temperature  $T$ . In this limit, the instantaneous dissociation rate  $k_d(\infty)$  is equal to the equilibrium dissociation rate denoted as  $k_d$ . Note that  $k_d = \bar{k}_d n_X$ , where  $n_X$  is the number density of inert gas.

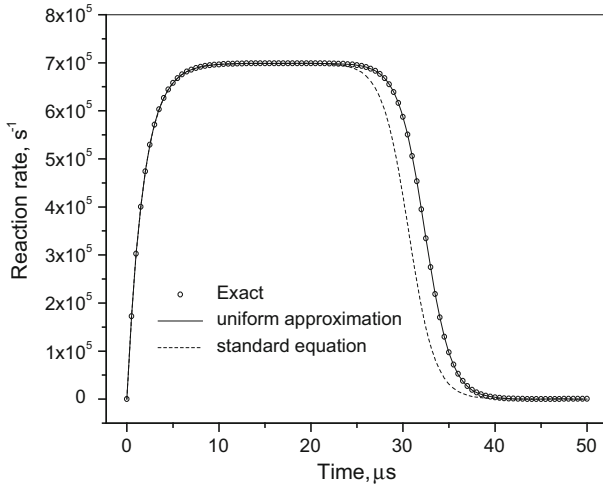
Knowing the concentrations of molecules and atoms, we may calculate their ratio. The  $A^2/M$  ratio is obtained as a function of time

$$\frac{A_a(t)^2}{M_a(t)} = \frac{k_d(t)}{k_r} \left[ \frac{\xi(t)^2 - 1}{\xi(t)^2 \coth^2[y(t)] - 1} \right] \quad (21)$$

Apparently, the  $A_a(t)^2/M_a(t)K_{eq}$  ratio increases monotonically with time from zero to unity (see Fig. 2). These results are in complete accord with the conclusions available in the literature [1, 2, 10–12], and are verified experimentally.

The theory developed provides analytical expressions for the concentrations of reagents and products to calculate the reaction rate in an analytical form. Substituting Eqs. (12) and (17) into Eq. (5) we get

$$K(t) = \frac{k_d(t) \xi(t)^2}{1 + (\xi(t)^2 - 1) \cosh^2[y(t)]} \quad (22)$$



**Fig. 3** Time dependence of the reaction rate  $K(t)$  of shock-heated  $O_2$  in Ar. The heat-bath temperature is 10,000 K and the initial vibrational temperature is 300 K

As follows from Eq. (22), the reaction rate is equal to the instantaneous dissociation rate only at short times when the squared hyperbolic cosine is almost equal to unity (when the ratio  $k_r A(t)^2/M(t)$  is small as compared with  $k_d(t)$ ). At long times, the reaction rate tends to zero according to the exponential law

$$K(t) \approx k_d(\infty) \frac{4\xi(\infty)^2}{\xi(\infty)^2 - 1} \exp(-\xi(\infty)k_d(\infty)t) \tag{23}$$

In this limit,  $M(t)$  and  $A(t)$  tend to their equilibrium concentrations and stop to depend on time. Therefore, the  $\dot{M}(t)$  and  $\dot{A}(t)$  derivatives vanish. Note that  $K(t)$  decreases with the damping rate  $\xi(\infty)k_d(\infty)$ , where parameter  $\xi(\infty)$  is found from Eqs. (13) and (20). As follows from Fig. 3, the reaction rate increases rapidly at short times to reach the “plateau”, where the approximate equality  $K(t) \approx k_d(\infty)$  holds for a time scale exceeding the induction period usually associated with vibrational relaxation. Then, the reaction rate decreases exponentially to zero at long times. In this limit, the last term of Eq. (5) comes into effect so that the  $A(\infty)^2/M(\infty)$  ratio should be equal to  $K_{eq}$  in the steady-state condition.

### 3 Exact analytical solution to Eq. (1) in the model of strong collisions

Now we have to answer the question of how the instantaneous dissociation rate  $k_d(t)$  or the flux coefficient  $k_d(t)M(t)$  vary with time. The concentration of atoms is calculated from Eq. (12) and given in terms of  $k_d(t)$ . In turn, the concentration of molecules may be found from Eq. (17). The flux coefficient may be readily calculated using the available vibrational populations. However, these may be determined from Eq. (1), in which the species concentrations are involved as the time-dependent functions. A

possibility to solve this problem in the analytical form depends on the fact whether information on the concentration of reagents and products may be extracted from an independent source. If this is the case, we may both determine the populations under certain assumptions of the type of rate coefficients and calculate the flux coefficient. The real concentrations of atoms and molecules are then estimated using the above procedure. By this means, we ascertain more qualitatively the nature of the dissociation–recombination process because its theory is formulated in the completely analytical form, at least, for this particular case.

It is generally believed that the dissociation–recombination process starts with an initial fast transient that has duration on the order of the vibrational relaxation time during which there is a negligible change in concentrations but the populations approach a distribution which is close to a solution of the steady-state master equation. During the steady-state phase of the relaxation process, the evolution of the system is interpreted within the usual phenomenological rate equation similar to Eq. (2) but with the constant coefficients  $k_d$  and  $k_r$  [1–6, 10–12].

A phenomenological rate equation has been repeatedly derived from the general master equation. It corresponds to the steady-state phase of the relaxation process. These results may be obtained in some other way without using the  $t \rightarrow \infty$  limit but assuming that the dissociation and recombination rates depend on the vibrational quantum number in a prescribed manner. The simplest method to derive Eq. (7) from Eqs. (1)–(4) is to suggest that the dissociation and recombination rates depend on  $n$  as

$$k_{n \rightarrow c} = k_d \quad \text{and} \quad k_{c \rightarrow n} = \rho_n k_r \quad (24)$$

The dissociation is assumed to follow from the entire manifold of internal states with a mean dissociation rate. When the dissociation rate is independent of  $n$ , the recombination one is proportional to the equilibrium thermal distribution where  $k_r$  is the proportionality factor. In other words, two atoms create a molecule in each single event of recombination. Actually, Eq. (24) is the model of strong collisions for the dissociation–recombination process. In the framework of this model, the transition rate between discrete states,  $n \rightarrow n'$ , is proportional to the probability to find a molecule in the final state  $n'$  independent of its initial state

$$k_{n \rightarrow n'} = v_* \rho_{n'}, \quad (25)$$

where  $v_*$  is the effective collision frequency of molecules  $M$  with inert atoms  $X$ .

The assumptions made allow us to greatly simplify master equation (1)

$$\frac{dM_n}{dt} = -(v_* + k_d) M_n(t) + \rho_n [v_* M(t) + k_r A(t)^2] \quad (26)$$

When the reaction is absent, the master equation becomes particularly simple

$$\frac{dM_n}{dt} = -v_* [M_n(t) - \rho_n M(t)] \quad (27)$$



Note that the equation of this type is called either the Krook–Bhatnager–Gross equation in the kinetic theory of gases [13, 14] or the simple relaxation approximation. Since the effective collision frequency is independent of the vibrational quantum number,  $\nu_*$  may be determined so that the relaxation equation for the mean vibrational energy,  $\langle\langle E(t) \rangle\rangle$ , written in terms of approximation (27), coincided with the phenomenological one. The phenomenological relaxation equation for  $\langle\langle E(t) \rangle\rangle$  is of the form [15]

$$\frac{d}{dt} \langle\langle E(t) \rangle\rangle = -\frac{\langle\langle E(t) \rangle\rangle - \langle E \rangle_T}{\tau_V}, \quad (28)$$

where  $\langle E \rangle_T$  is the mean thermal energy of vibrations at temperature  $T$  and  $\tau_V$  is the mean time of the vibrational relaxation. From Eq. (27) we get

$$\frac{d}{dt} \langle\langle E(t) \rangle\rangle = -\nu_* [\langle\langle E(t) \rangle\rangle - \langle E \rangle_T] \quad (29)$$

Comparing Eq. (28) with (29) yields  $\nu_* = 1/\tau_V$ .

Summing up the both sides of Eq. (26) over all  $n$ , we obtain the equation similar to Eq. (2) but with the constant coefficients  $k_d$  and  $k_r$ . Thus, the concentrations of reagents and products are the available time-dependent functions, provided by Eqs. (9) and (11) with  $\kappa_d = k_d$  and  $\kappa_r = k_r$ . It is a matter of direct verification to prove that a solution to Eq. (26) is given by

$$M_n(t) = \rho_n M_s(t) + \left[ \frac{M_n(0)}{M(0)} - \rho_n \right] M(0) \exp \left[ - \left( \frac{1}{\tau_V} + k_d \right) t \right] \quad (30)$$

As evident from this relation, the memory of the initial condition is forgotten after the time period on the order of  $\tau_V/(1+k_d\tau_V)$  and the populations relax to the equilibrium values such as  $\rho_n M_s(t)$  in line with the input assumption.

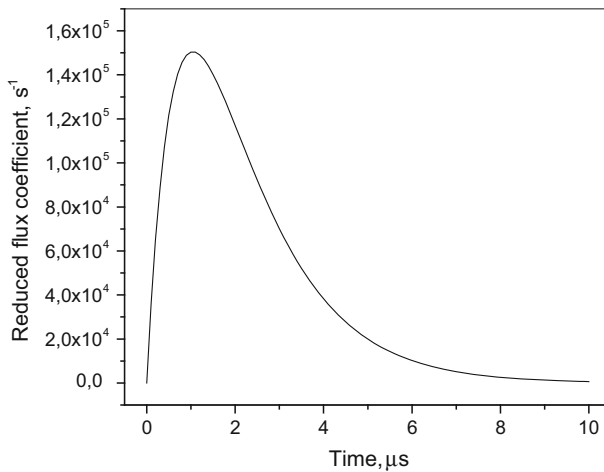
Equations (3) and (30) lead then to the expression for the instantaneous dissociation rate

$$k_d(t) = k_d(\infty) + [k_d(0) - k_d(\infty)] \frac{M(0)}{M_s(t)} \exp \left[ - \left( \frac{1}{\tau_V} + k_d \right) t \right] \quad (31)$$

Remember that  $k_d(\infty) = k_d$ . Consider now the first case where the molecules are initially “cold” and the temperature of the inert gas  $X$  increases instantaneously up to high  $T$  (as, e.g., in shock waves). The initial value of  $M_n(0)/M(0)$  is provided by the vibrational Boltzmann distribution at the initial temperature  $T_i$ . We also assume a thermal equilibrium for the translational and rotational degrees of freedom of the molecules at  $T$ . Then the initial dissociation rate obeys the equation

$$k_d(0) = \sum_n \rho_n(T_i) k_{n \rightarrow c}(T) \quad (32)$$

In this case,  $k_d(\infty)$  is higher than  $k_d(0)$  and the instantaneous dissociation rate increases monotonously from  $k_d(0)$  to  $k_d(\infty)$ . Due to collisions between the species  $M$  and  $X$ , the molecules gain internal energy from the heat bath over a period of time, i.e., the system relaxes by collisional  $T \rightarrow V$  energy transfer.



**Fig. 4** Typical time evolution of the reduced flux coefficient  $R(t)/M(0)$

Let us consider the case, where the inert-gas heat bath is initially cold (and remains cold at temperature  $T$ ) while the internal energy of the molecules is instantaneously raised by a laser pulse of short duration. Now the vibrational degrees of freedom are characterized by the temperature  $T_i$  so that  $T_i > T$ . Obviously,  $k_d(0)$  exceeds  $k_d(\infty)$  and the instantaneous dissociation rate decreases monotonously from  $k_d(0)$  to  $k_d(\infty)$ . Now the molecules lose internal energy to the heat bath over a period of time, so that the relaxation consists of the  $V \rightarrow T$  energy transfer.

We denote the flux coefficient  $k_d(t)M(t)$  by  $R(t)$ . Hence,  $R(t)$  is of the form

$$R(t) = k_d(\infty)M_s(t) + [k_d(0) - k_d(\infty)]M(0) \exp\left[-\left(\frac{1}{\tau_V} + k_d(\infty)\right)t\right] \quad (33)$$

The behavior of  $R(t)$  with time is plotted in Fig. 4. Let the heat bath temperature differ slightly from the initial one of the vibrational degrees of freedom. Then the flux coefficient decreases exponentially from  $k_d(0)M(0)$  to zero during the time roughly equal to that of the vibrational relaxation. In this case, the  $M_n(t)/M(t)$  distribution is not very different from the initial thermal distribution. When  $T \gg T_i$ , this distinction is considerable. The high-lying energy levels are excited by strong collisions and  $R(t)$  starts to increase sharply with time to reach a maximum within the time period on the order of  $\tau_V/(1 + k_d\tau_V)$ . At long times, the flux coefficient tends to its asymptotic limit.

## 4 System

As an illustration, we consider the dissociation–recombination process of shock-heated oxygen molecules, highly diluted in argon heat bath. The parameters of the model system are the ones used by Kiefer and Hajduk [16] for the  $O_2 + Ar$  and  $O + O + Ar$  collisions. The vibrational bias parameter is  $\lambda = 3.5$ . The initial temperature

is 300 K and the temperature of the heat bath is 10,000 K. We set both the argon concentration to  $1.28 \times 10^{17} \text{ cm}^{-3}$  to agree with the shock-tube study of Wray [17] and the initial concentration of molecules to  $2.56 \times 10^{15} \text{ cm}^{-3}$ . The molecule is modeled as a truncated harmonic oscillator with 27 vibrational levels spaced by 2255.7 K and the dissociation energy is 58,920 K. The calculated values for the necessary parameters are  $k_d = 7.0 \times 10^5 \text{ s}^{-1}$  and  $k_r = 3.5 \times 10^{-20} \text{ cm}^3 \text{ s}^{-1}$ . The frequency of collisions is  $1.64 \times 10^8 \text{ s}^{-1}$  and the mean vibrational time equals 1.76  $\mu\text{s}$  of the Camac study [18].

## 5 Summary and conclusions

In the present work, we have analyzed the  $M + X \rightleftharpoons 2A + X$  reaction, derived the analytical expressions for the concentrations of molecules and atoms, and determined the reaction rate, functionally dependent on the instantaneous dissociation rate. Comparing the results of Eqs. (12), (17), (21) and (22) with numerically exact calculations attests that the uniform approximation provides the highly accurate values and is independent of many aspects of interest, such as the functional  $k_d(t)$  form, the damping rates of this function, and the input parameters. In all the cases studied, a relative difference was no more than 0.5%. Theoretically, the above results are a successful example of solving the nonlinear, differential equation of type (6) by the method of standard equation.

The main interest of our study was to express the species concentrations through the instantaneous dissociation rate. When the latter is known as a function of time, the theory allows a comparison between the calculated and the experimental values. Actually, an inverse problem may be stated. Based on physical considerations, we give  $k_d(t)$  as a function of time and of several fitting parameters whose values are then determined using experimental species concentrations. Planning these studies in future, we have proposed an instructive example in Sect. 3, where the functional form of  $k_d(t)$  was found by means of a simple physical model. Within this model of strong collisions, we have presented the exact, analytical solution to the master equation.

An old topic of chemical kinetics concerns the conditions under which a phenomenological rate equation is obeyed. In this connection it is useful to pay attention to the difference in solutions provided by Eqs. (9) and (12). As follows from the expression for  $A_s(t)$ , the concentration of atoms only increases with time to reach from below the equilibrium  $A_s(\infty)$  value. The effect of decreasing atom concentration, following the depletion of non-decomposed molecules, is fully absent in the phenomenological model. For the general case, the time-dependent concentration of atoms may have a maximum. Actually, this effect is described by solution to  $A_a(t)$ , because the concentration of atoms follows a temporal change in the dissociation rate. According to numerical calculations, this behavior is typical of the case where  $T_i \gg T$  and the equilibrium constant for the reaction is not too large.

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