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State-to-state dissociation rate coefficients in electronically excited diatomic gases

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Abstract

In the present Letter, state dependent dissociation rate coefficients in diatomic gases with non-equilibrium vibrational and electronic excitation and chemical reactions are studied. A widely used Treanor–Marrone model is generalized to take into account state-to-state vibrational and electronic distributions. The influence of electronic excitation on the rate of dissociation from various electronic states of CO molecules is estimated.
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1. Introduction

Recent experimental and theoretical results on non-equilibrium kinetics in high temperature and high enthalpy flows [1] proved the existence of a strong coupling between the processes of internal energy relaxation and chemical reactions. Moreover, accurate calculations of the rate coefficients of vibrational energy exchange and dissociation [2–6] show that in a wide temperature range the rates of these processes are comparable, and therefore multi-temperature models based on various quasi-stationary distributions over vibrational energy are not valid. This fact has lead to a rapid development of state-to-state modelling of kinetics, dynamics and transport processes in real gas flows [1,7]. The state-to-state approach describes flow kinetics and dynamics in terms of gas velocity, temperature and populations of all vibrational levels of molecular species. These flow parameters are found from the momentum and energy conservation equations solved simultaneously with the equations of detailed vibrational–chemical kinetics. The production terms in these last equations are determined by the state-to-state rate coefficients of all strongly non-equilibrium processes, in particular, different vibrational energy transitions and chemical reactions.

Modelling of the state-to-state rate coefficients of vibrational energy exchanges and dissociation is a crucial point for the correct solution of master equations. Since experimental data on the state dependent rate coefficients are limited by a low temperature range (see for instance [8,9]), theoretical models for the rates of non-equilibrium physical–chemical processes are of great importance. The most reliable data on the cross-sections and rate coefficients of vibrational transitions and dissociation are obtained by means of quantum trajectory calculations [2–4,10] and quasi-classical dynamical approach [6,11,12]. However, a direct use of these accurate but extremely time consuming methods in computational fluid dynamics is possible only by exploiting computing grid technologies which at present time are still in their infancy (see [13–15] for the description of grid computing tools). A review of more simple analytical and semi-empirical models for the state-to-state and multi-temperature rate coefficients is given in [1,16].

While there exist several models of dissociation rate coefficients taking into account state-to-state vibrational distributions, no analytical model taking into account

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electronic excitation has been developed up to now. Nevertheless, recent studies of non-equilibrium kinetics show an important role of electronic states in the formation of vibrational distributions [17–20] and radiation from non-equilibrium regions [18–20].

The aim of this Letter, is to develop a simple model of dissociation rate coefficients which permits to account for electronically excited states. For this purpose, the Treanor–Marrone model is generalized for diatomic gases with non-equilibrium vibration–electronic excitation.

2. Model description

In the present study, a non-equilibrium reacting gas flow is considered under the following condition:

$$\tau_{\rm tr} \sim \tau_{\rm rot} \ll \tau_{\rm vibr} \sim \tau_{\rm electr} \sim \tau_{\rm react} \sim \theta, \tag{1}$$

where $\tau_{\rm tr}$, $\tau_{\rm rot}$, $\tau_{\rm vibr}$, $\tau_{\rm electr}$, $\tau_{\rm react}$ are the characteristic times of translational, rotational, vibrational and electronic relaxation and chemical reactions, and θ is the mean time of macroscopic parameters change. Such a hierarchy of characteristic times represents the basis for the development of the state-to-state approach, which apparently provides the most appropriate description of the kinetics and gas dynamics in the majority of strongly non-equilibrium flows [1,7].

Under condition (1), in the zeroth order approximation of the generalized Chapman–Enskog method, the particle distribution functions over velocity and rotational energy are found, respectively, in the form of the Maxwell and the Boltzmann distributions whereas the highly non-equilibrium state-to-state distributions over vibrational and electronic energy as well as concentrations of chemical species must be obtained as solutions of master equations [18,19].

Dissociation of a diatomic molecule $A_{c\alpha i}$ (c is the chemical species, α and i are the electronic and vibrational levels correspondingly) in a collision with a partner A_d which does not change its internal state during the collision proceeds through the reaction

$$A_{c\alpha i} + A_d = A_f + A_g + A_d, \tag{2}$$

where A_f and A_g are the atomic reaction products. We suppose that atoms A_f and A_g appear in their ground electronic states and therefore, only those molecular electronic states which dissociation energies are approximately the same: $D^c_\alpha \approx D_c\ \forall\alpha$ are included to our consideration.

In the state-to-state approach, the rate coefficient $k^{{\rm diss},d}_{c\alpha i}$ of reaction (2) is introduced for each vibrational and electronic levels of chemical species c. In the inviscid Euler regime $k^{{\rm diss},d}_{c\alpha i}$ is defined as a dissociation cross-section $\sigma^{{\rm diss},d}_{c\alpha i}$ averaged with the Maxwell–Boltzmann distribution over velocity and rotational energy. In the Euler regime, the state-to-state rate coefficients depend only on the gas temperature T while in the Navier–Stokes regime they depend also on the non-equilibrium electronic–vibrational level populations $n_{c\alpha i}$ and velocity divergence $\nabla\cdot\mathbf{v}$ [21].

Since the reliable data on the cross-sections of process (2) taking into account excited electronic states are not available in the literature, theoretical modelling of coefficients $k^{{\rm diss},d}_{c\alpha i}$ is required. In this study, similarly to [22–24], we express the state-to-state dissociation rate coefficient in terms of the thermal equilibrium rate coefficient $k^{{\rm diss},d}_{c,{\rm eq}}$ and a non-equilibrium factor $V_{c\alpha i}$

$$k^{{\rm diss},d}_{c\alpha i} = V_{c\alpha i} k^{{\rm diss},d}_{c,{\rm eq}}. \tag{3}$$

The thermal equilibrium dissociation rate coefficient $k^{{\rm diss},d}_{c,{\rm eq}}$ can be found using the Arrhenius law

$$k^{{\rm diss},d}_{c,{\rm eq}} = AT^n \exp\left(-\frac{D_c}{kT}\right), \tag{4}$$

where parameters A and n are found by fitting the rate coefficients to the experimental data. In the general case these parameters depend on the chemical species c and d of the reaction reagents.

In order to calculate the non-equilibrium factor $V_{c\alpha i}$ one can introduce a dimensionless ratio

$$P^d_{c\alpha i} = \frac{k^{{\rm diss},d}_{c\alpha i} n_{c\alpha i}}{k^{{\rm diss},d}_c n_c}, \tag{5}$$

which can be considered as a probability that a molecule c dissociates from the electronic α and vibrational i levels. In expression (5), $n_c = \sum_{\alpha i} n_{c\alpha i}$ is the number density of c species, an averaged dissociation rate coefficient $k^{{\rm diss},d}_c$ reads

$$k^{{\rm diss},d}_c = \frac{1}{n_c}\sum_{\alpha i} n_{c\alpha i} k^{{\rm diss},d}_{c\alpha i}.$$

Since coefficients $k^{{\rm diss},d}_{c\alpha i}$ do not depend on the electronic-vibrational level populations $n_{c\alpha i}$, then

$$k^{{\rm diss},d}_{c\alpha i} = k^{{\rm diss},d}_c \frac{P^d_{c\alpha i}}{n_{c\alpha i}/n_c} = k^{{\rm diss},d}_{c,{\rm eq}} \frac{P^d_{c\alpha i}}{(n_{c\alpha i}/n_c)^{\rm eq}}. \tag{6}$$

Under thermal equilibrium conditions the populations of electronic–vibrational levels follow the Boltzmann distribution:

$$\left(\frac{n_{c\alpha i}}{n_c}\right)^{\rm eq} = \frac{s^{c\alpha}_i s^c_\alpha}{Z^c_{\rm el}(T) Z^{c\alpha}_{\rm vibr}(T)} \exp\left(-\frac{\varepsilon^c_\alpha + \varepsilon^{c\alpha}_i}{kT}\right), \tag{7}$$

where $\varepsilon^{c\alpha}_i$, ε^c_α are the vibrational and electronic energies of corresponding states, $s^{c\alpha}_i$, s^c_α are the vibrational and electronic statistical weights, k is the Boltzmann constant, $Z^{c\alpha}_{\rm vibr}$, $Z^c_{\rm el}$ are the thermal equilibrium partition functions:

$$Z^{c\alpha}_{\rm vibr} = \sum_i s^{c\alpha}_i \exp\left(-\frac{\varepsilon^{c\alpha}_i}{kT}\right),$$

$$Z^c_{\mathrm{el}} = \sum_\alpha s^c_\alpha \exp\left(-\frac{\varepsilon^c_\alpha}{kT}\right).$$

The commonly accepted Treanor–Marrone dissociation model [22] assumes that a molecule dissociates with equal probability in any collision which has a sufficient translational energy, and that decomposition proceeds preferentially from the high vibrational levels. Generalizing this model to the conditions of electronic excitation, we also admit preferential dissociation from the highly located vibrational levels of each electronic state. In this case, the probability $P^d_{c\alpha i}$ can be written in the form:

$$P^d_{c\alpha i} = C\frac{n_{c\alpha i}}{n_c}\mathscr{M}\left(D_c - (\varepsilon^c_\alpha + \varepsilon^{c\alpha}_i)\right)F^d_{c\alpha i}, \tag{8}$$

here $\mathscr{M}(D_c - (\varepsilon^c_\alpha + \varepsilon^{c\alpha}_i))$ is the fractional number of collisions with line-of-center relative energy more than $D_c - (\varepsilon^c_\alpha + \varepsilon^{c\alpha}_i)$ and $F^d_{c\alpha i}$ is the probability that the molecule c at the vibrational level i and electronic level α, when colliding in a sufficiently energetic collision, will dissociate. The constant C is found from the normalizing condition

$$\sum_{\alpha i} P^d_{c\alpha i} = 1. \tag{9}$$

The probability $F^d_{c\alpha i}$ in (8) reads

$$F^d_{c\alpha i} = C_1 \exp\left(-\frac{D_c - (\varepsilon^c_\alpha + \varepsilon^{c\alpha}_i)}{kU_d}\right), \tag{10}$$

where U_d is an additional parameter which has a dimension of a temperature and describes how rapidly the dissociation probability decreases for low levels, C_1 is the constant independent of α and i.

For the Maxwell distribution over velocities

$$\mathscr{M}\left(D_c - (\varepsilon^c_\alpha + \varepsilon^{c\alpha}_i)\right) = C_2 \exp\left(-\frac{D_c - (\varepsilon^c_\alpha + \varepsilon^{c\alpha}_i)}{kT}\right), \tag{11}$$

constant C_2 is also independent of α and i.

Finally, using expressions (5)–(11) and a common assumption that the parameter U_d does not depend on the partner d in reaction (2), i.e., that $U_d = U\ \forall d$, one can rewrite the non-equilibrium factor in the form:

$$V_{c\alpha i}(T,U) = Z^c_{\mathrm{el}}(T)\exp\left(\frac{\varepsilon^{c\alpha}_i + \varepsilon^c_\alpha}{k}\left[\frac{1}{T} + \frac{1}{U}\right]\right) \times \left[\sum_\beta s^c_\beta \exp\left(\frac{\varepsilon^c_\beta}{U}\right)\frac{Z^{c\beta}_{\mathrm{vibr}}(-U)}{Z^{c\beta}_{\mathrm{vibr}}(T)}\right]^{-1}. \tag{12}$$

This factor represents a state-to-state vibration–electronic-dissociation coupling factor for preferential dissociation from highly excited electronic and vibrational levels. If only the ground electronic state of a molecule c is taken into account, expression (12) reduces to a state dependent vibration-dissociation coupling factor obtained in [23,24]

$$V_{ci}(T,U) = \frac{Z^c_{\mathrm{vibr}}(T)}{Z^c_{\mathrm{vibr}}(-U)}\exp\left(\frac{\varepsilon^c_i}{k}\left[\frac{1}{T} + \frac{1}{U}\right]\right). \tag{13}$$

In the limit case $U = \infty$ the non-equilibrium factor (12) takes the form:

$$V_{c\alpha i}(T) = Z^c_{\mathrm{el}}(T)\exp\left(\frac{\varepsilon^{c\alpha}_i + \varepsilon^c_\alpha}{kT}\right)\left[\sum_\beta \frac{s^c_\beta L_{c\beta}}{Z^{c\beta}_{\mathrm{vibr}}(T)}\right]^{-1}, \tag{14}$$

where $L_{c\beta}$ is the number of excited vibrational levels of the molecular species c at the electronic state β. Formula (14) describes a coupling factor for non-preferential dissociation which proceeds with equal probability from any electronic and vibrational level. When only the ground electronic state is considered, the non-equilibrium factor (14) corresponds to the coupling factor of the well known Hammerling model for non-preferential dissociation [25].

The choice of the parameter U is rather important for a correct prediction of the non-equilibrium dissociation rate coefficients. It can be obtained by fitting the rate coefficients to the experimental results or the results of more rigorous calculations. Thus in [24] it is shown that for nitrogen under moderate and high temperature conditions, values $U = 3T$ and $U = D/(6k)$ provide a satisfactory agreement of the state-to-state dissociation rate coefficients to the results of the quasi-classical dynamical approach. Unfortunately the experimental data or exact quantum calculations of the state dependent dissociation rate coefficients in gases with electronic excitation are not available. Consequently further analysis of coefficients $k^{\mathrm{diss},d}_{c\alpha i}$ for different U values can give only some qualitative estimations.

3. Results and discussion

Let us consider carbon monoxide molecule and its electronic states $X^1\Sigma$, $a^3\Pi$, $A^1\Pi$ which contribute to the reaction

$$\mathrm{CO}(X^1\Sigma, a^3\Pi, A^1\Pi) + M = C(^3P) + O(^3P) + M. \tag{15}$$

The state-to-state rate coefficients of this reaction have been calculated on the basis of formulas (12) and (13) taking into account three electronic states and only the ground state $X^1\Sigma$, respectively. Parameters in the Arrhenius law (4) are those given by Park et al. [26]. Different values of the parameter U have been studied: $U = 3T$, $U = D/(6k)$, $U = D/(3k)$ for preferential dissociation and $U = \infty$ which corresponds to the non-preferential dissociation model. These values are chosen accordingly to the most commonly employed values of the Treanor–Marrone model parameter U [16].

Fig. 1 presents the temperature dependence of the state-to-state rate coefficients $k^{\mathrm{diss}}_{\mathrm{CO},\mathrm{X}^1\Sigma,i}$ of CO dissociation from the ground electronic level calculated using expressions (12) and (13) in the temperature range 5000–25 000 K for preferential ($U = 3T$) and non-preferential ($U = \infty$) dissociation models. One can see that all rate coefficients increase with temperature, the rate of dissociation from highly located vibrational states exceeds noticeably the corresponding rate for lower lying states.

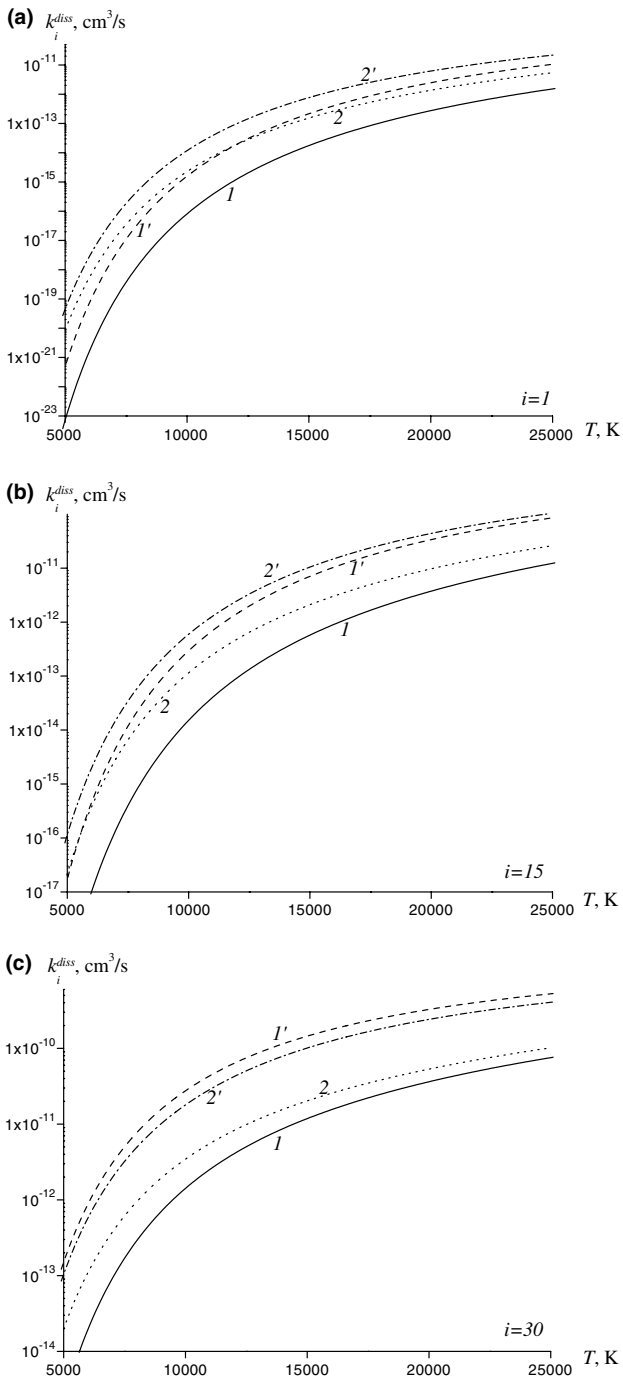

Fig. 1. Rate coefficient $k^{\mathrm{diss}}_{\mathrm{CO},\mathrm{X}^1\Sigma,i}$ of dissociation from the ground electronic level as a function of temperature. (a): $i = 1$; (b): $i = 15$; (c): $i = 30$. Curves 1, 2 are obtained using formula (12); $1', 2'$: with formula (13). $1, 1'$: $U = 3T$; $2, 2'$: $U = \infty$.

Taking into account several excited electronic levels leads to a considerably lower rate of dissociation from the ground electronic state for all vibrational levels in the whole temperature range (if the same model of dissociation is applied). It is a consequence of the internal energy redistribution between electronic states. Indeed, the thermal equilibrium vibrational level populations of the state $\mathrm{X}^1\Sigma$ (see (7)) depend on the electronic partition function Z^c_{el} which is determined by the number of excited electronic states.

When several electronic states are involved to the process (15), the rate of non-preferential dissociation remains higher compared to the rate of preferential dissociation for all vibrational levels, although this discrepancy decreases significantly with i. If only the ground electronic level contributes to the reaction (15), for low and intermediate vibrational levels the rate coefficients corresponding to non-preferential dissociation exceed the ones obtained for preferential dissociation whereas for high vibrational states this relationship becomes inverse.

In Fig. 2 the non-equilibrium factor $V_{\mathrm{CO},\mathrm{X}^1\Sigma,i}$ is given for the same case as the rate coefficients in the previous figure but for a wider temperature range: $T = 1000$–50 000 K. Consideration of the coupling factors instead of the rate coefficients is quite useful because it allows to avoid the uncertainty introduced by the empirical form of the Arrhenius law and eliminate its temperature limitation. It is interesting to emphasize a different behaviour of the factor $V_{\mathrm{CO},\mathrm{X}^1\Sigma,i}$ for various vibrational levels. While for highly located states the coupling factor decreases with temperature, for low and intermediate levels its temperature dependence may have a non-monotonous character.

Fig. 3 demonstrates the temperature dependence of the ratio

$$K = \frac{k^{\mathrm{diss}}_{\mathrm{CO},i}}{k^{\mathrm{diss}}_{CO,\mathrm{X}^1\Sigma,i}} = \frac{V_{\mathrm{CO},i}}{V_{\mathrm{CO},\mathrm{X}^1\Sigma,i}}, \tag{16}$$

where $k^{\mathrm{diss}}_{\mathrm{CO},\mathrm{X}^1\Sigma,i}$ and $k^{\mathrm{diss}}_{\mathrm{CO},i}$ are calculated taking into account three electronic levels and only the ground one, respectively. Different curves correspond to various values of the parameter U. It should be noted that ratio (16) does not depend on the vibrational level (see formulas (13) and (12)). One can notice a weak temperature dependence of K for the case of non-preferential dissociation ($U = \infty$): at low temperatures $K \approx 5$, and at the high temperature limit $K \to 2$. In the cases $U = D/(3k)$ and $U = D/(6k)$ the factor K still remains a slow varying function of T whereas for $U = 3T$ a significant variation of K has been found. At low temperatures values of K achieve several hundreds, and with temperature rising

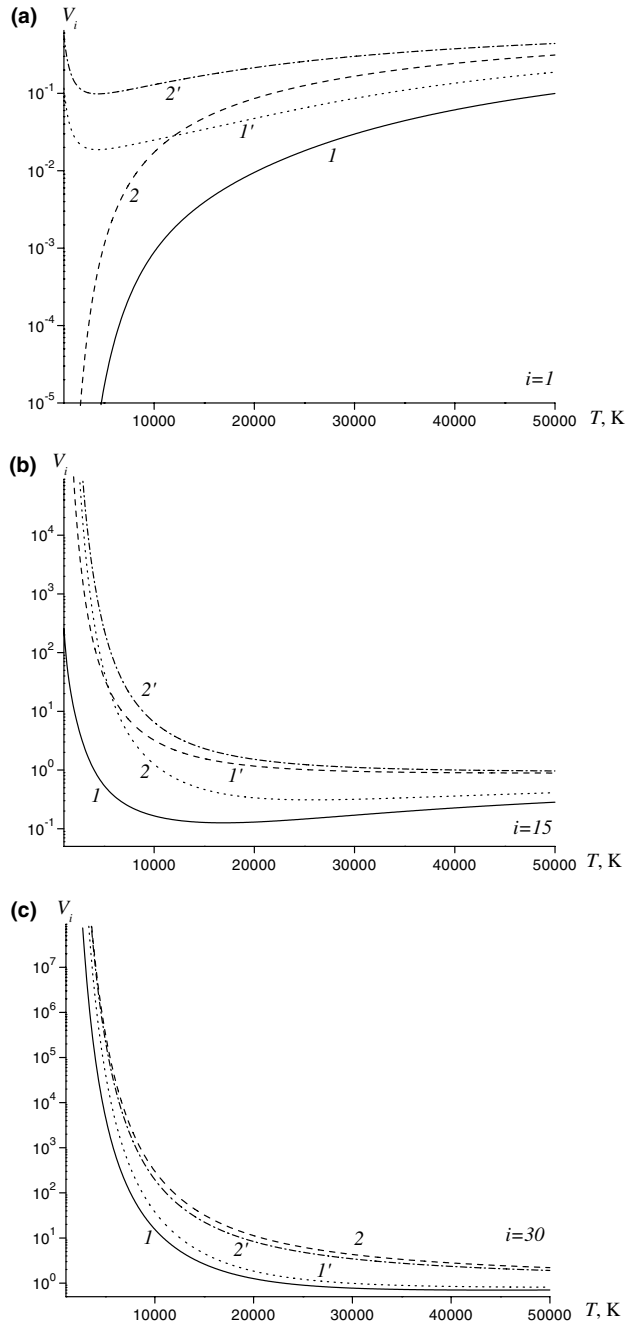

Fig. 2. Non-equilibrium factor $V_{CO,X^1\Sigma,i}$ of dissociation from the ground electronic level as a function of temperature. See Fig. 1 for explanations.

they decrease and become close to the values obtained for non-preferential dissociation.

In Fig. 4 the influence of the parameter U on the dissociation rate coefficient $k^{diss}_{CO,X^1\Sigma,1}$ is shown. The highest value of the coefficient is obtained in the case of non-preferential dissociation, the value $U = D/(6k)$ provides a slowest rate of dissociation at $T > 7000$ K since it corresponds to preferential dissociation from very highly located vibrational levels.

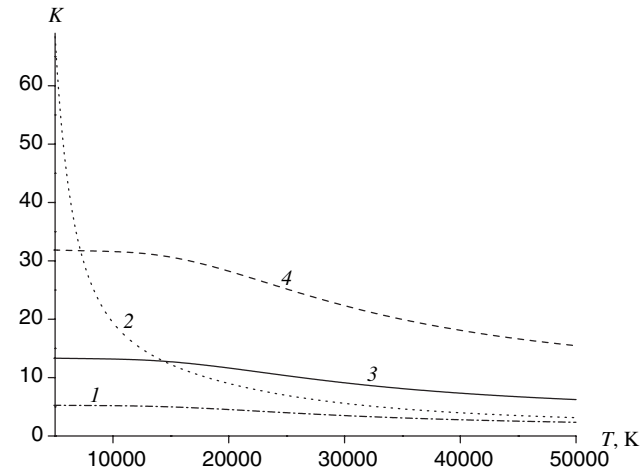

Fig. 3. Ratio K of the rate coefficients calculated using formulas (12) and (13). (1): $U = \infty$; (2): $U = 3T$; (3): $U = D/(3k)$; (4): $U = D/(6k)$.

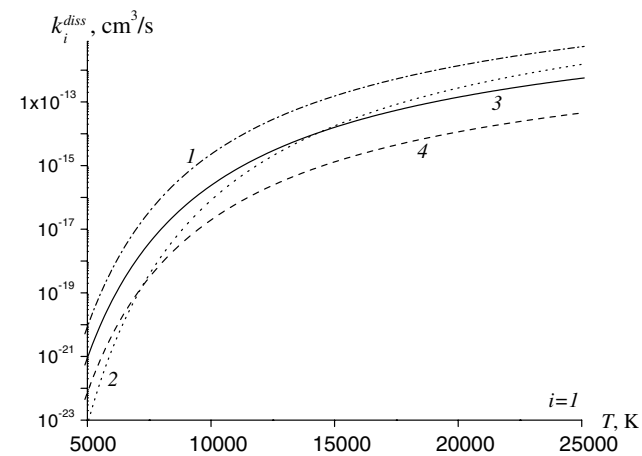

Fig. 4. Rate coefficient $k^{diss}_{CO,X^1\Sigma,1}$ as a function of temperature. (1): $U = \infty$; (2): $U = 3T$; (3): $U = D/(3k)$; (4): $U = D/(6k)$.

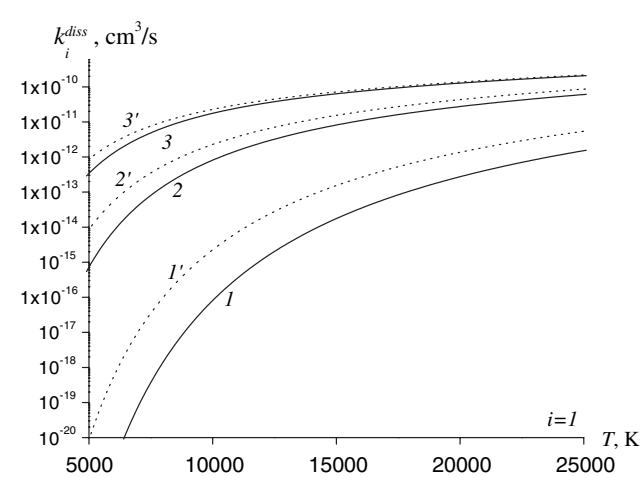

Fig. 5. Rate coefficients $k^{diss}_{CO,\alpha,1}$ of dissociation from different electronic levels. Curves 1–3 correspond to the electronic states $X^1\Sigma$, $a^3\Pi$, $A^1\Pi$. (1)–(3): $U = 3T$; 1′–3′: $U = \infty$.

A comparison of the dissociation rate coefficients for various electronic states (for $i = 1$) is presented in Fig. 5. It is seen that the rate coefficients increase considerably for high electronic levels, the discrepancy between coefficients calculated using the preferential and non-preferential dissociation models decreases with α and becomes rather weak for the level $A^1\Pi$. It is interesting to note that the dissociation rate coefficients for electronic levels possessing a higher degree of degeneracy (like the level $a^3\Pi$ which statistical weight is equal to three), can be comparable and even exceed in some cases the rate coefficients for more energetic but non-degenerated levels.

4. Conclusion

In this Letter, a simple model of the state-to-state dissociation rate coefficients taking into account electronic excitation is proposed and applied for the calculation of the rate coefficients of dissociation from several electronic levels of CO. Different values of the model parameter U are tested, and the influence of the dissociation model on the rate coefficients is estimated. In particular, it is shown that consideration of several electronic levels can reduce the rate coefficients for the ground electronic state by 10–100 times.

Further validation of this model can be performed using rigorous quantum calculations or experimental results on the dissociation cross-sections in electronically excited gases (which are still not available in the literature). Nevertheless, the model improves the existing semi-empirical models, and can be used in the computational fluid dynamics.

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