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Detailed kinetic of CO₂ dissociation and C ionization: application to atmospheric Martian entries

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Abstract. In order to calculate global rate coefficients for atmospheric Martian entries situations, a detailed kinetic model using a state-to-state approach is developed for two important processes: dissociation/recombinaison of CO₂ and ionization/recombinaison of Carbon. The behavior of the species involved is governed by the general balance equation including forward and backward elementary processes whose rate coefficients are in part based on experimental data. Extrapolation methods are used when necessary. During the population densities time-evolution, a quasi steady state can be identified: a global rate coefficient can be derived only during this state. The rates therefore obtained are fitted under a modified Arrhenius law and some of them are finally compared with experimental results.

1. Introduction

The atmospheric entry of a spacecraft or a probe constitutes the more critical step of a spatial flight as illustrated by the dramatic crash of Columbia in 2003. During this phase, the incident flow reaching the fuselage is hypersonic ($v \approx 10 \text{ km s}^{-1}$). Owing to the high compressibility of the flow, the pressure and temperature undergo a steep increase inside a shock layer near the surface: a complex chemistry is then activated which leads to the formation of excited and ionized species. This gas \rightarrow plasma transition enhances not only the convective flux resulting from the high temperature levels concerned, but also the radiative and chemical parts of the total flux. As a result, the spacecraft or probe surface can be damaged. The amount of reactive species and their inner excitation degree are the key points of the plasma-wall interaction. Accordingly, a clear identification of the underlined chemistry is crucial.

In CORIA, we have already contributed to state-to-state plasma studies devoted to air chemistry [1]. The study of CO₂-N₂ plasma flows in relation with Martian entries is now in progress in the continuity of the previous ones. Two problems to be addressed shortly are identified:

- **dissociation and recombination of CO₂.** CO₂ is the main species of Martian atmosphere: dissociation phenomena occur through state-to-state thermal excitation of vibrational modes. At high temperature, these phenomena are far from being completely understood: one of the objectives of the present study is to give an insight into the dissociation mechanism of CO₂ by developing such a state-to-state approach. The approach adopted lead also to estimates of the recombination rate coefficient.



- **ionization and recombination of C.** At high temperature, atoms like C, N and O can produce ions. The global ionization process takes place through the state-to-state electronic excitation then ionization of atoms. Once again, developing a detailed approach can provide fruitful information not only about ionization, but also for recombination. Such an approach is developed only for C in a first step.

In the following, dissociation/recombination of CO₂ and ionization/recombination of C are studied through the elaboration of relevant state-to-state models.

2. State-to-state models

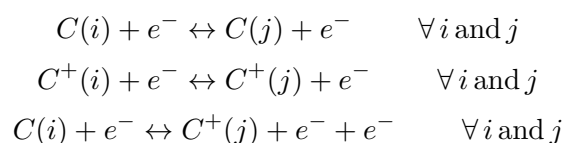
2.1. Dissociation/recombination of CO₂

CO₂ is a molecule with three modes of vibration: a symmetric and an asymmetric non degenerate stretching modes and a doubly degenerate bending mode whose characteristic energies are classically written $h\nu_1$, $h\nu_3$ and $h\nu_2$ respectively. In a first approximation, CO₂ is assumed to behave like a harmonic oscillator. In addition, the energy diagram is assumed totally independent from the Fermi resonance between the first and the second modes. This procedure leads to account for 120 vibrational levels to simulate the dissociation/recombination.

In our conditions, the stepwise vibrational excitation leading to dissociation results from vibration-translation elementary processes. Only mono-quantum transition are taken into account in the same mode in a first approximation. Blauer's data [2] are used: they provide the rate value for the vibrational de-excitation from the first to the ground state in each mode and they are then extrapolated until the dissociation continuum by using the SSH theory [3]. Finally, Boltzmann and Guldberg & Waage equilibrium laws are used to derive rate coefficients for vibrational excitation and dissociation. In the present context, CO₂, CO and O are considered as the main collisional partners.

2.2. Ionization/recombination of C

All the excited states of C (225 levels) and the first eight states of C⁺ given by the NIST database [4] are taken into account. The temperature ranges being wide, C atoms can be excited or ionized from any excited state according to:



where electron is assumed to be the main collision partner.

Three different types of transition are possible for the excitation/deexcitation of C or C⁺: optically allowed, parity forbidden and spin forbidden transitions. The Drawin's cross sections set is used [5] to calculate the corresponding reaction rates. The backward reaction rates are derived from the detailed balance principle by using the Boltzmann and Saha equilibrium laws.

2.3. Approach

Our calculations are systematically performed in constant pressure p and temperature T conditions: in this context, global rate coefficients for either dissociation/recombination or ionization/recombination can be derived. This leads to some difficulties which can be relatively easily addressed. For instance, during a strong ionization phase resulting from an initial strong non equilibrium, electron number increases very fast: accordingly, pressure and temperature cannot be both taken as constant. Indeed, if pressure and temperature are constant, the global density remains unchanged which is incompatible with an ionization condition. This situation requires therefore necessarily a plasma volume which can evolve in time. Even when

the ionization is strong, electron number inside the volume considered can freely change under constant pressure and temperature. A global ionization rate can then be derived.

The pressure and temperature are first chosen, then the complete equilibrium composition is calculated. In case the CO₂ dissociation rate is studied, a higher CO₂ density is initially chosen with respect to the density derived from the equilibrium calculation. The same procedure is adopted concerning the initial C density in the case of the C global ionization rate coefficient determination. Recombination rates can be studied by taking the complementary situations.

Time-dependent calculations are performed in our approach. They are based on classical balance equations treatment without neither energy nor particles exchange whose general form is:

$$\frac{d[X_i]}{dt} = \left(\frac{\partial[X_i]}{\partial t} \right)_{Coll.} = G - L \quad (1)$$

where G and L are the gain and loss terms respectively of the source term. These terms take into account the elementary processes discussed in previous sections and the equations set formed owing to the number of species considered is solved using the DVODE library [6].

With this temporal approach, we can therefore follow for instance the time-evolution of the ratios:

$$K_{CO_2}(t) = -\frac{\frac{d[CO_2]}{dt}}{[CO_2] \frac{p}{k_B T}} \quad \text{and} \quad K_C(t) = -\frac{\frac{d[C]}{dt}}{[C][e^-]} \quad (2)$$

during CO₂ dissociation (left) or C ionization (right). These ratios correspond exactly to rate coefficients when they are not evolving with time: in this case, excited states constitute an intermediate reservoir ensuring the transfer of particles from the CO₂ or C ground states to the continuum of dissociation or ionization respectively. This transient situation is named “quasi steady state” because it lasts while the amount of CO₂ or C particles is high enough. After, the ratios are evolving once again until the new equilibrium is reached.

The previous approach can be easily adapted to the case of recombination situations. Then it is worth to follow the ratios:

$$K'_{CO_2}(t) = \frac{\frac{d[CO_2]}{dt}}{[CO][O] \frac{p}{k_B T}} \quad \text{and} \quad K'_C(t) = \frac{\frac{d[C]}{dt}}{[C^+][e^-]^2} \quad (3)$$

which correspond to the recombination rate coefficients during the quasi steady-state.

3. Results

3.1. CO₂ dissociation/recombination

Figure 1 displays the population densities evolution in time obtained during the dissociation of CO₂ for $p = 10^5$ Pa and $T = 6000$ K. The initial density of CO₂ is too high with respect to the equilibrium density corresponding to these conditions: the dissociation starts approximately when $t = 10^{-11}$ s through the excitation of higher energy levels. Around 10^{-4} s, a steep decrease of the number density of the CO₂ states take place just before a temporary situation where these densities are almost constant. This situation corresponds to the quasi steady-state mentioned in the previous section: a dissociation rate coefficient can be derived from the present calculations only during this state. After, the population number densities evolve again owing to instantaneous departure from equilibrium until it is reached.

Left ratio of 2 is used to derive the global dissociation rate coefficient during the quasi steady-state. The values obtained do not depend on the pressure level, therefore on the total density. The influence of the total density is only observed on time-evolutions owing to its indirect

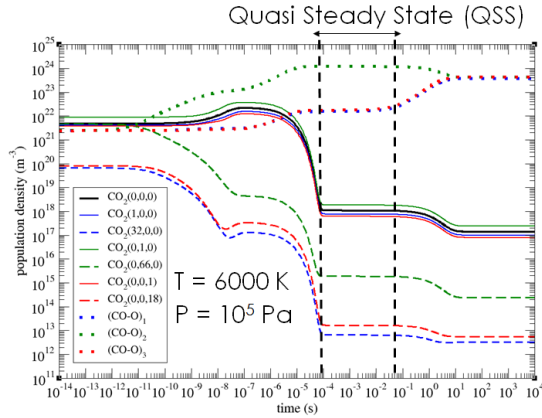


Figure 1. Population densities time-evolution for a typical CO₂ dissociation situation.

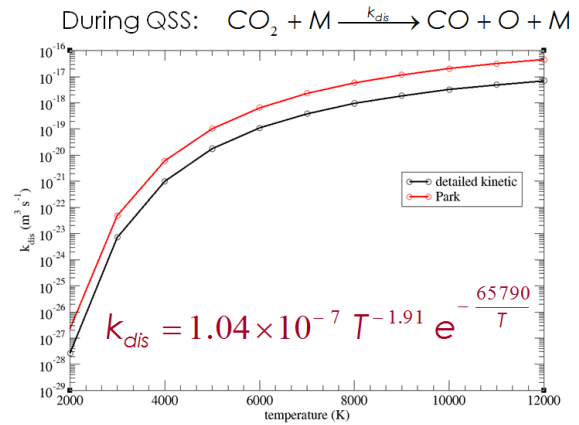


Figure 2. Temperature-dependent CO₂ dissociation global rate coefficient.

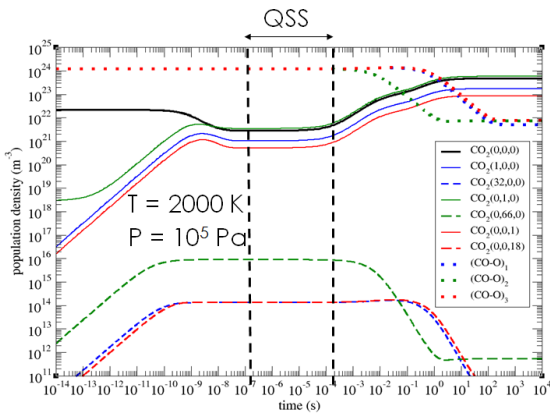


Figure 3. Population densities time-evolution for a typical CO₂ recombination situation.

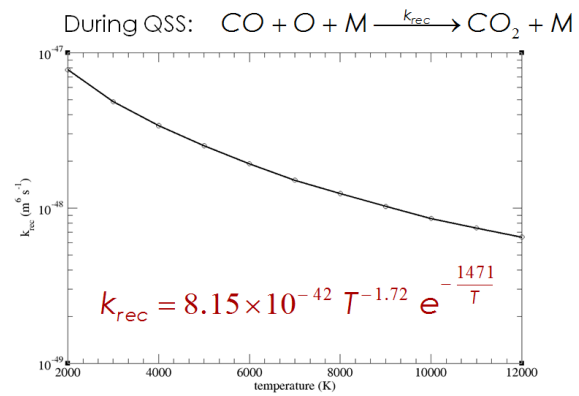


Figure 4. Temperature-dependent CO₂ recombination global rate coefficient.

influence on the collision frequency: a higher density means a higher collision frequency which leads to faster evolution. The quasi steady state is therefore obtained earlier.

A quasi steady-state is observed whatever the conditions adopted for p and T : therefore, a rate coefficient can be systematically derived. Over the range [2000K, 12000K] for T , the results illustrated by figure 4 put forward a logical increase with T of the rate coefficient more important at moderate temperature. These results can be easily fitted by the following modified Arrhenius form:

$$k_{dis} = 1.04 \times 10^{-7} T^{-1.91} e^{-\frac{65790}{T}} \quad (4)$$

where the characteristic temperature in the exponential term is remarkably close to the dissociation one (64000 K).

This figure displays also the temperature-dependent rate coefficient stated by Park [7] whose chemical model is often implemented in high enthalpy flows calculations related to Martian atmospheric entries. Park's assumptions obviously underestimate the rate coefficient. Our

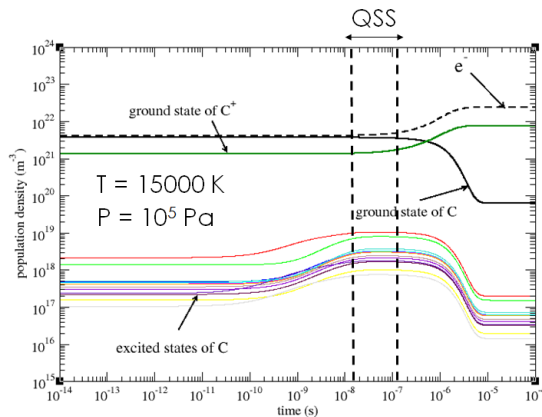


Figure 5. Population densities time-evolution for a ionization situation.

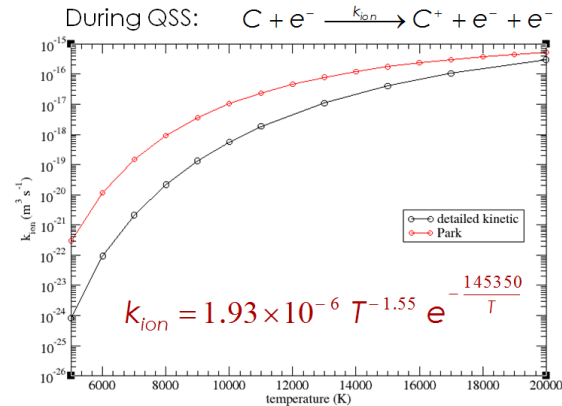


Figure 6. Global rate coefficient for C ionization by electronic impact.

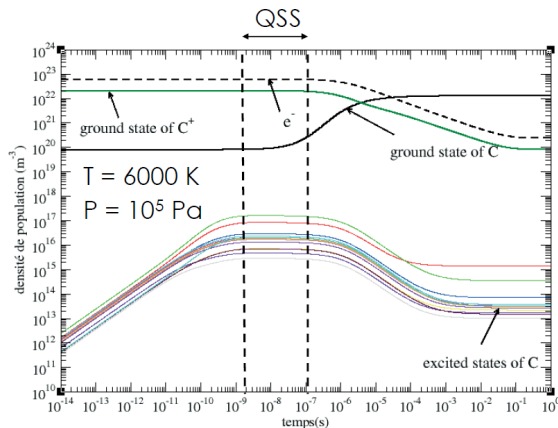


Figure 7. Population densities time-evolution for a recombinaison situation.

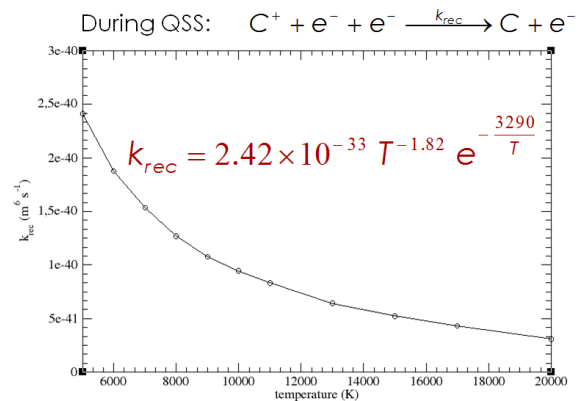


Figure 8. Global rate coefficient for C ionization by electronic impact.

values are indeed very close to the ones obtained experimentally in shock tube experiments [8, 9].

Figure 3 displays the results of the temporal evolutions of densities for the same pressure level, but for $T = 2000$ K. The recombination is obvious. The three phases put forward previously for the dissociation case are observed once again. In particular, the quasi steady-state is clearly visible. The rate coefficient derived during this transient state is determined by the left equation 3. By generalizing these calculations, one obtains the global rate coefficient as a function of T displayed by figure 4 and very well fitted under the following modified Arrhenius form:

$$k_{rec} = 8.15 \times 10^{-42} T^{-1.72} e^{-\frac{1471}{T}} \quad (5)$$

The characteristic temperature involved in the exponential term is close to 0: this result is logic since the recombination is a process without any threshold.

3.2. C ionization/recombination

The characteristics previously pointed out for the case of CO_2 are also observed for C as a result of the discussion of section 2.3. Figure 5 displays the time-evolution of densities in the case $p =$

10^5 Pa and $T = 6000$ K. Figure 6 illustrates the evolution with T of the global rate coefficient for ionization of C. Once again, these results are well fitted by a modified Arrhenius law with:

$$k_{ion} = 1.93 \times 10^{-6} T^{-1.55} e^{-\frac{145350}{T}} \quad (6)$$

Figure 6 displays also the values given by Park. We can observe an identical evolution, but with higher discrepancies, except at high temperature where both series converge.

The typical evolution in time of population densities in the case of a recombination situation is displayed on figure 7. The quasi steady-state is more difficult to be observed: nevertheless, its existence cannot be disputed. Using right equation 3, the global recombination rate can be deduced during the quasi steady-state. As illustrated by figure 8, they are once again very well fitted by a modified Arrhenius law such that:

$$k_{rec} = 2.42 \times 10^{-33} T^{-1.82} e^{-\frac{3290}{T}} \quad (7)$$

4. Conclusion

This work addresses a state-to-state approach dedicated to the determination of global rate coefficients for the dissociation or the recombination of CO_2 and the ionization or recombination of C involved in the Martian atmospheric entries chemistry. This state-to-state approach put forward the existence of a quasi steady-state where global rate coefficients can be derived with relevance. Their values follow closely modified Arrhenius forms which can be easily implemented in fluid mechanics numerical codes.

The results displayed in the present communication are preliminary. Some improvements have indeed to be performed and are already in progress:

- **CO_2 dissociation/recombination.** Collisions with CO_2 molecules can induce cross modifications of the vibrational excitation between the three modes. They have to be taken into account. Multiquanta transitions occur also during collisions and will be implemented.
- **C ionization/recombination.** The results obtained depend on the cross sections set chosen to model the chemistry. Other sets will be shortly tested, in particular the one derived from the HULLAC package [10].

Finally, it is worth to notice that a backward rate coefficient is systematically derived from the forward one using directly the related equilibrium law. This approach is not necessarily relevant owing to the departure of equilibrium for the excited states during quasi steady-state. The present approach will give interesting point of view about this question.

Acknowledgments

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