Electron-vibration relaxation in oxygen plasmas

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An ideal chemical reactor model is used to study the vibrational relaxation of oxygen molecules in their ground electronic state, $X^3\Sigma_g^-$, in presence of free electrons. The model accounts for vibrational non-equilibrium between the translational energy mode of the gas and the vibrational energy mode of individual molecules. The vibrational levels of the molecules are treated as separate species, allowing for non-Boltzmann distributions of their population. The electron and vibrational temperatures are varied in the range $[0 - 20000]$ K. Numerical results show a fast energy transfer between oxygen molecules and free electron, which causes strong deviation of the vibrational distribution function from Boltzmann distribution, both in heating and cooling conditions. Comparison with Landau-Teller model is considered showing a good agreement for electron temperature range $[2000 - 12000]$ K. Finally analytical fit of the vibrational relaxation time is given.

I. INTRODUCTION

The study of non-equilibrium relaxation in weakly ionized molecular plasmas is of great interest to the scientific community. Examples of applications include: atmospheric entry [1–3], optical diagnostics, discharges [4], plasma assisted combustion [5], material processing, just to name a few. This work is concerned with the study of non-equilibrium phenomena in high speed plasma flows relevant to the entry into Earth's atmosphere, in particular the electron-oxygen energy transfer will be considered, which study, in our opinion, has been largely overlooked by the aerothermodynamic community. Previous works on electron cooling by oxygen molecules in upper atmosphere can be found in the Ref. [6–9] and more recently by Jones *et al.* [10]

This research is at the interface between computational chemistry and computational fluid dynamics and aims at the development of reduced models based on microscopic theory and applying them to the macroscopic scale. Previously published research efforts were focused on the characterization of the $N_2(X^1\Sigma_g^+)$ kinetics, resulting from the interaction with $N(^4S^o)$ atoms [11–13] and free electrons [14–16]. In this paper, by using a state-to-state (STS) kinetic approach, we concentrate on the study of the energy exchange between electrons and vibrational energy for $O_2(X^3\Sigma_g^-)$ molecules. In particular, we are interested in the study of non-equilibrium regimes characterized by low free electron temperature (< 10000 K). In hypersonic applications, in fact, the electrons formed by collision impact between heavy

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particles are relatively cold, and the average energy of the electrons is bounded by the heavy particle energy.

Due to the lack of a dipole moment, low-energy electron-impact cross sections for direct excitation of vibrational states of homo-nuclear molecules, like oxygen or nitrogen, are, in general, negligible. However, the vibrational excitation in the case of N_2 and O_2 molecules can also proceed *via* the formation of an intermediate **negative ion complex, the so-called** resonant processes. A well known example is the N_2^- resonance for nitrogen molecule. The study of $\text{N}_2(\text{X } ^1\Sigma_g^+)$ excitation by electron-impact has been the object of considerable investigation both from the theoretical [14, 17–23] and experimental [24–26] point of view. For oxygen molecules, the minimum of the potential energy curve of O_2^- lies below that of O_2 and the position of the resonance is therefore very close to the cross section threshold [27–29]. As result, the electron-vibration energy transfer in oxygen could be an efficient process at low temperature even if the magnitude of corresponding cross sections are not as large as those for nitrogen.

This work addresses the study of the vibrational energy transfer processes in an ideal chemical reactor filled with molecular oxygen and free electrons. Dissociation is neglected. In this reactor, cold oxygen molecules at room temperature, seeded with small amount of free electrons, are suddenly heated by several thousand degrees Kelvin driving the gas toward a strong non-equilibrium condition. The present investigation is devoted to the in-depth study of the relaxation of oxygen $\text{O}_2(\text{X } ^3\Sigma_g^-)$ molecules in presence of free electrons. Our proposed model relies on state-specific reaction rate coefficients of an *ab-initio* database developed as part of the Phys4Entry database [30]. The published results will serve as a benchmark for validation of more approximate theories reduced order models. Furthermore, the insights gained by the analysis of oxygen excitation will serve as guidelines for the development of reduced models. As first step in this direction we have extracted macroscopic relaxation rate parameters for the vibrational energy transfer of oxygen molecules in an electron gas. The derived parameters can be readily used in fluid-dynamic codes for the modeling non-equilibrium plasma flows.

The manuscript is organized as follow: Section II contains the physical model and the computational method used; In section III A the effect of the multi-quantum transitions is studied and in Section III B the results in the relaxation time formalism are presented. Conclusions are drawn in Section IV.

II. PHYSICAL MODEL

We wish to investigate the vibrational excitation of oxygen molecules, in their electronic ground state $\text{X } ^3\Sigma_g^-$, when subjected to sudden heating/cooling in an ideal chemical reactor, filled with hot/cold electrons. We make the following assumptions: (i) The mixture electron– O_2 is supposed to be kept in a isothermal bath at constant free-electron temperature T_e ; (ii) Electrons are considered in equilibrium according to a Maxwell-Boltzmann distribution at temperature T_e , with a corresponding pressure given by,

$$p_e = n_e k_B T_e, \quad (1)$$

where n_e is the electron number of particles per unit volume and k_B the Boltzmann constant; (iii) At the beginning of the numerical experiment, the population of the vibrational energy levels of the oxygen molecules is assumed to follow a Maxwell-Boltzmann distribution at

v	ϵ_v	v	ϵ_v	v	ϵ_v
0	0.000	14	2.435	28	4.280
1	0.196	15	2.587	29	4.382
2	0.388	16	2.735	30	4.476
3	0.573	17	2.881	31	4.565
4	0.756	18	3.024	32	4.651
5	0.937	19	3.164	33	4.730
6	1.117	20	3.301	34	4.794
7	1.291	21	3.436	35	4.847
8	1.461	22	3.568	36	4.898
9	1.629	23	3.696	37	4.938
10	1.796	24	3.821	38	4.960
11	1.960	25	3.942	39	4.976
12	2.122	26	4.059	40	4.987
13	2.281	27	4.172	41	4.994

TABLE I: Calculated vibrational levels of $\text{O}_2(\text{X } ^3\Sigma_g^-)$ molecule for rotational level $j = 1$. Energies are given in eV.

the internal temperature $T_v^0 \neq T_e$; (iv) The volume of the chemical reactor is kept constant during the experiment and the thermodynamic system is closed (no mass exchange with surrounding environment); (v) The electronic excitation and ionization processes are not considered. The kinetic processes included in the numerical simulations are the vibrational-excitations (VE) by electron-impact, *i.e.*:

where $v, w \in \mathcal{V} = \{0, \dots, 41\}$ are vibrational levels supported by the potential energy curve of electronic ground state of O_2 for $j = 1$ rotational level. The list of the vibrational energy levels ϵ_v used in this work is given in Table I.

The vibration relaxation process of the molecules in a chemical reactor can be described by means of a kinetic or STS approach. The vibrational distribution function (vdf) of the oxygen molecules, $n_v(t)$, in a particular energy level v is then obtained by solving a system of master equations (ME),

$$\frac{dn_v}{dt} = n_e \sum_{w \in \mathcal{V}} [k_{w,v} n_w - k_{v,w} n_v], \quad v \in \mathcal{V}, \quad (3)$$

where the electron impact rate coefficients $k_{v,w}(T_e)$ have been calculated from cross sections reported in Refs. [27, 28] assuming a Maxwell-Boltzmann distribution for free electrons. For electron energies of interest to this study, the excitation of the oxygen molecules, Eq. (2), proceeds *via* the formation of negative ion O_2^- , with subsequent de-excitation. In calculating the cross sections, the $^2\Pi_g$, $^2\Pi_u$, $^4\Sigma_u^-$, $^2\Sigma_u^-$ resonant states have been included. Some results for $k_{v,w}$ are shown in Fig. 1 for mono- and multi-quantum vibrational transitions.

A different approach to modeling vibrational energy relaxation is due to Landau and Teller (LT) [31] and it is based on a number of assumptions that are in general valid for simple harmonic oscillator molecules. Within the LT formalism, the relaxation parameter,

FIG. 1: Electron- O_2 vibrational excitation rate constants for mono- ($w - v = 1$, plot on the left) and multi-quantum ($w - v = 10$, plot on the right) transitions for $j = 1$. The results are taken from Refs. [27, 28]

τ_e , is defined as the characteristic time of a first order dynamical system response. The time evolution of oxygen vibrational energy E_{vib} , given by:

$$E_{vib}(t) = \sum_{v \in \mathcal{V}} n_v(t) \epsilon_v, \quad (4)$$

is governed by the solution of first-order differential equation:

$$\frac{dE_{vib}}{dt} = \frac{E_{vib}^* - E_{vib}}{\tau_e}, \quad (5)$$

where E_{vib}^* is the equilibrium vibrational energy, at temperature T_e , defined by

$$E_{vib}^* = \sum_{v \in \mathcal{V}} n_v^*(T_e) \epsilon_v, \quad (6)$$

where $n_v^*(T_e)$ is the equilibrium O_2 vdf.

III. ELECTRON-VIBRATIONAL ENERGY TRANSFER

In this section, the STS model, presented above, will be used to study the relaxation kinetics of the vibrationally excited states in the isothermal and isochoric reactor for a wide range of conditions: $T_e \in [500 - 20000]$ K and $T_v^0 \in [100 - 20000]$ K. Three observables are calculated and discussed: population distributions, averaged vibrational energy and internal relaxation times.

A. Effect of Multi-quantum transitions

The objective of this section is the analysis of the electron-vibrational energy **transfer** in cooling ($T_v^0 > T_e$) and heating conditions ($T_v^0 < T_e$). To this end, the vdf of the O_2 molecules at different times in the relaxation is plotted in Fig. 2 (solid blue line), for two specific test-cases. In both cases the initial distribution of the vibrational energy levels is

FIG. 2: Time-evolution of normalized O₂ vibrational distribution function for two different cases in heating, $T_v^0 < T_e$ (left hand side), and cooling, $T_v^0 > T_e$ (right hand side). Solutions with full set of multi-quantum transitions allowed (solid blue line), $\Delta v = 20$ (red dashed line) and $\Delta v = 10$ (green dot-dashed) are shown.

assumed to be populated according to a **Boltzmann distribution** at temperature T_v^0 , which is shown in Fig. 2 as a straight solid line (at $t = 0 \mu s$). Both cases analyzed are characterized by: a mixture number density of $n = 3.2 \cdot 10^{22}$ particles/m³, with molar fractions of 0.995 and 0.005 for O₂(X³Σ_g⁻) and e⁻ respectively. Since dissociation is not considered, the molar fraction stays unchanged throughout the simulation.

As the time passes the distribution of the excited states is distorted, causing an overpopulation (underpopulation) of the tail in the heating (cooling) case. As the relaxation proceeds further, the population of the excited states slowly relaxes until equilibrium of the vibrational and free electron temperature is achieved. It is interesting to note that the population of the low-lying excited states is very well **described by a Boltzmann distribution** for most of the relaxation. This gives us confidence on the ability of reduced order model to be able to understand the energy relaxation dynamics.

In order to study the effect of multi-quantum transitions in the dynamics of reaction in (2), we have repeated the simulation including a reduced number of processes. To this end, we have introduced the parameter Δv , which limits the maximum energy transfer allowed by the inelastic collision process, *i.e.* such that:

$$|v - w| \leq \Delta v, \quad (7)$$

in this way only a subset of the whole set STS processes being included in the simulation. **A similar approach has been developed for nitrogen in the papers in the Refs. [13, 14].** Throughout this paper, by “*full*” solution we indicate the results obtained with the entire set of vibrational levels, *i.e.* $\Delta v = 42$. In Fig. 2 and 3 we show the results for the vdf and for the vibrational energy in two opposite cases of heating and cooling and we compare the behavior of the $\Delta v = 20$ (red dashed line) and $\Delta v = 10$ (green dot-dashed) solutions with respect to full solution (solid blue line).

In the heating case, we note a strong depletion of the high-lying vibrational levels, which are scarcely populated. This is due to a reduced efficiency of the electrons driven processes, and to their low population densities. Although the population of the high-lying vibrational levels obtained with $\Delta v = 20$ and $\Delta v = 10$ depart from the full solution, the time required to reach equilibrium seems to be unaffected. This can be observed in the time evolution of vibrational energy on the right side of Fig. 3, where the solutions for $\Delta v = 20$ and $\Delta v = 10$

FIG. 3: Time-evolution of vibrational energy corresponding to the plots in Fig. 2.

practically follow **the full** solution. The consideration made in the heating case apply to the cooling case, for which the extent of non-equilibrium seems reduced. For this reason it is not further discussed.

In order to better quantify the effect of multi-quantum transitions on the relaxation process, we have calculated the differences between the full solution and the corresponding solution with different Δv by introducing the error estimation ε such that,

$$\varepsilon = \max \frac{|E_{vib}^{full}(t) - E_{vib}^{\Delta v}(t)|}{E_{vib}^{full}(t)}, \quad (8)$$

where E_{vib}^{full} and $E_{vib}^{\Delta v}$ are the solutions of Eq. (4) for the full and Δv case starting with the same initial conditions. Plots in Fig. 4 summarize the results of calculations for the case $\Delta v = 20$ and $\Delta v = 10$. Two aspects can be noted: (i) As expected, in the same conditions T_e and T_v the error increases as the number of allowed transitions decreases, $\varepsilon(\Delta v = 10) > \varepsilon(\Delta v = 20)$; (ii) The error increase as the difference $|T_e - T_v|$ increase. In facts as the number of multi-quantum jumps is reduced the system needs more time to reach the equilibrium respect to the full simulation. Moreover, the maximum errors are observed in cooling, *i.e.* $T_v > T_e$, where the cooling of the tail of the vdf requires multi-quantum jumps. In particular the worse case is recorded for $\Delta v = 10$ and $T_v > T_e$. So that in order to implement a reduced model on the vibrational level it should be used only for $|T_e - T_v| \approx 0$ and to include at least $\Delta v = 20$ gap between vibrational levels.

B. Relaxation time formalism

In this section, we focus on relaxation time formalism and in particular we would like to assess the validity of the LT model, by comparing its results with ME predictions. Both approaches have been introduced in Section II.

In the ME approach, to extract the relaxation time, we solve the full STS system in Eq. (3), for fixed T_e and T_v^0 . From the vibrational populations of O_2 , $n_v(t)$, we compute the O_2 averaged vibrational energy, defined by Eq. (4), and then we fit $E_{vib}(t)$ with the analytical solution of LT equation, Eq. (5), using τ_e as an external parameter. In order to make the results independent of the electron density the results are provided in terms of $p_e \tau_e$. The second approach relies on the LT relaxation formula to define, τ_e . In this case,

FIG. 4: Maximum error ε obtained in solving time evolution in the all ranges T_e and T_v for $\Delta v = 10$ (left hand side) and $\Delta v = 20$ (right hand side).

the relaxation time can be calculated as:

$$p_e \tau_{10} = \frac{k_B T_e}{k_{1,0}(T_e) (1 - e^{-\theta/T_e})}, \quad (9)$$

where $k_{1,0}$ is the fundamental mono-quantum rate coefficient (*i.e.* the $v = 0$ curve in left hand side plot in Fig. 1) and $\theta = (\epsilon_1 - \epsilon_0)/k_B = 2282.01$ K is the characteristic temperature for O_2 . Time relaxation, in LT formalism, depends only on electron temperature. Results for both approaches are summarized in Fig. 5.

Plot on left hand side in Fig. 5 shows a comparison of the relaxation time, for the two cases discussed above, as a function of T_e , and for different initial vibrational temperatures, T_v^0 . At the first look, one may notice that as the relaxation time calculated from ME approach is T_v^0 -dependent. It is interesting to observe how the LT approximation gives reasonable values of the relaxation times for the wide range of electron temperatures 2000–12000 K. Obviously the simple LT expression cannot account for the influence of the initial vibrational excitation, which appears particularly important at high T_e .

In order to better visualize the results of relaxation time, in plot on the right-hand side of Fig. 5, the time evolution of the normalized vibrational energy obtained from ME and LT approaches have been compared for a specific test-case at fixed $T_e = 8000$ K and for different T_v^0 . Solid blue curves represent the ME solutions whereas dashed green lines refer to the LT model. The agreement between the two models is acceptable in particular for $T_v^0 = 5000, 10000$ K but at low and high T_v^0 LT fails to reproduce the correct behaviour of the system.

The $p_e \tau_e(T_e, T_v^0)$ relaxation times obtained from ME can be fitted by a polynomial function,

$$p_e \tau_e(T_e, T_v^0) = \sum_{n=0}^4 \sum_{m=0}^2 c_{n,m} T_e^n T_v^{0m}, \quad (10)$$

for T_e in the range [2000 – 20000] K and T_v^0 in the interval [0 – 20000] K. The coefficients

FIG. 5: **On the left:** Calculated $p_e \tau_e$ for different initial vibrational temperature T_v^0 (solid lines) compared with the Landau-Teller approximation (green dashed line). **On the right:** Time-evolution of normalized vibrational energy corresponding to electron temperature $T_e = 8000$ K for different initial vibrational temperature T_v^0 . Solid blue lines refer to the master equation solutions, whereas dashed green lines refer to the Landau-Teller results.

n \ m			
	0	1	2
0	2.418	$-2.660 \cdot 10^{-4}$	$1.015 \cdot 10^{-8}$
1	$-2.094 \cdot 10^{-3}$	$3.537 \cdot 10^{-7}$	$-1.153 \cdot 10^{-11}$
2	$7.174 \cdot 10^{-7}$	$-7.578 \cdot 10^{-11}$	$2.422 \cdot 10^{-15}$
3	$-4.511 \cdot 10^{-11}$	$4.435 \cdot 10^{-15}$	$-1.407 \cdot 10^{-19}$
4	$8.682 \cdot 10^{-16}$	$-8.131 \cdot 10^{-20}$	$2.610 \cdot 10^{-24}$

TABLE II: Coefficients $c_{n,m}$ for the two-dimensional fit for $p_e \tau_e$ in Eq. (10).

$c_{n,m}$ are given in Table II.

Finally, in Fig. 6 we show the comparison between the present results for $p_e \tau_e$ for oxygen and the corresponding results for nitrogen taken from Ref. [14]. From the figure it is easy to see how the vibrational relaxation of nitrogen molecules is significantly faster than the oxygen vibrational relaxation for temperature exceeding 7000-8000 K. This suggests the possible existence of non-equilibrium between the vibrational energies of molecular oxygen and nitrogen molecules, interacting with electron gas for condition of interest to hypersonic entry applications. However, it is important to notice that, to validity of this conclusion is limited only to the electron driven processes, considered in this analysis. Only a more comprehensive analysis including both electron and heavy particle driven processes will be able to shed some light on the existence of vibrational non-equilibrium between the vibrational energies of nitrogen and oxygen.

IV. CONCLUSIONS

We have performed extensive non-empirical calculations for oxygen energy transfer, which simulate an experiment conducted in an idealized isothermal chemical reactor, with free electrons as a collision partner. We solved the master equation for the entire vibrational structure of $O_2(X^3\Sigma_g^-)$ molecules allowing us to accurately describe the internal energy re-

FIG. 6: Comparison between calculated $p_e \tau_e$, as a function of the electron temperature, for oxygen (solid lines) and the corresponding results for nitrogen (dashed lines) [14] for two different initial vibrational temperatures.

laxation processes for a wide range of temperatures (0 - 20000 K). The state-to-state approach adopted in this work relies on the knowledge of the vibrational state-to-state transfer rate coefficients, computed as part of the *ab-initio* database developed at the University of Bari and part of the Phys4Entry project.

The modeling of the State-to-state processes in the chemical reactor has shown that the distribution of the vibrationally excited states strongly deviates from the equilibrium vibrational distributions, during the relaxation both in heating and cooling conditions. Although not considered here, this can have a strong influence on the chemical kinetics of reactive plasma flows, in particular where vibrationally favored reactions (*e.g.*, dissociation) play a role.

We have discussed the possibility to model the relaxation by a linear rate equation, the Landau-Teller formula, with a single relaxation time. The results obtained from the relaxation formalism and from the full kinetic model are compared to conclude that the former can be used with sufficient accuracy to model the vibrational energy relaxation in most cases of practical interest. Analytical fits of the relaxation time, that depends both on free electron and vibrational temperatures, has been provided.

Finally, we compared the characteristic relaxation time of $e\text{-N}_2(X^1\Sigma_g^+)$ and $e\text{-O}_2(X^3\Sigma_g^-)$ systems. We have shown that molecular nitrogen molecules relax at faster rates, especially for high temperatures.

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