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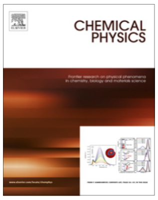

Electron-vibration relaxation in oxygen plasmas

V. Laporta [a,b,*], K.L. Heritier [c], M. Panesi [c]

[a] Istituto di Nanotecnologia, CNR, 70126 Bari, Italy
[b] Department of Physics and Astronomy, University College London, London WC1E 6BT, UK
[c] University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States

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ABSTRACT

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 [0–20,000] 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 [2000–12,000] K. Finally analytical fit of the vibrational relaxation time is given.

1. 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 Refs. [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 ($< 10,000$ K). In hypersonic applications, in fact, the electrons formed by collision impact between heavy 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 homonuclear 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 $N_2(X^1\Sigma_g^+)$ excitation by electron-impact has been the object of considerable investigation both from the theoretical [17–22,14,23] 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 [29,27,28]. 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

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* Corresponding author at: Istituto di Nanotecnologia, CNR, 70126 Bari, Italy.
E-mail addresses: vincenzo.laporta@nanotec.cnr.it (V. Laporta), kheritie@illinois.edu (K.L. Heritier), mpanesi@illinois.edu (M. Panesi).

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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 $O_2(X^3\Sigma_g^-)$ 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 2 contains the physical model and the computational method used; In Section 3.1 the effect of the multi-quantum transitions is studied and in Section 3.2 the results in the relaxation time formalism are presented. Conclusions are drawn in Section 4.

2. Physical model

We wish to investigate the vibrational excitation of oxygen molecules, in their electronic ground state $X^3\Sigma_g^-$, 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,

$$p_e = n_e k_B T_e, \tag{1}$$

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 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.:

$$e + O_2(X^3\Sigma_g^-; v, j) \rightleftarrows e + O_2(X^3\Sigma_g^-; w, j), \quad \text{(VE)} \tag{2}$$

where $v,\ w \in \mathcal{V} = \{0, \ldots, 41\}$ 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 1.

Table 1
Calculated vibrational levels of $O_2(X^3\Sigma_g^-)$ molecule for rotational level $j = 1$. Energies are given in eV.

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

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),

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

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, 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:

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

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

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

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

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

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

3. 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: $T_e \in [500\text{—}20,000]$ K and $T_v^0 \in [100\text{—}20,000]$ K. Three observables are calculated and discussed: population distributions, averaged vibrational energy and internal relaxation times.

3.1. 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 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 $t = 0$ µs). Both cases analyzed are characterized by: a mixture number density of $n = 3.2 \times 10^{22}$ particles/m^3, with molar fractions of 0.995 and 0.005 for $O_2(X^3\Sigma_g^-)$ and e^- respectively. Since dissociation is not considered, the molar fraction stays unchanged throughout the simulation.