MITIGATION OF ELECTRON REMOVAL IN NONEQUILIBRIUM ATMOSPHERIC PRESSURE AIR PLASMAS

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Abstract

We present experimental data and kinetic modeling on the effect of vibrationally driven mitigation of electron-ion recombination and electron attachment in electron beam sustained atmospheric pressure dry air plasmas. Time-resolved electron density measurements in e-beam excited air plasmas accompanied by kinetic modeling of the main electron production and removal processes are shown. In the experiments, nonequilibrium vibrational excitation is maintained by optical excitation of carbon monoxide, a few percent of which is seeded into the air, using a carbon monoxide laser and subsequent vibration energy transfer to oxygen and nitrogen. The experimental results are consistent with a model that assumes rapid vibrationally induced detachment of electrons from CV and vibrationally induced heating of the electrons to temperatures on the order of 5000 K, thus effectively mitigating the effect of electron attachment and electron-ion recombination, respectively.

Introduction

Sustaining large-volume plasmas in atmospheric pressure air presents a challenging problem. Among the most critical technical issues that have to be addressed to resolve this problem are the plasma power budget and stability. Numerous aerospace applications such as supersonic flow control, supersonic combustion control, and nonequilibrium MHD propulsion require an ability to initiate and sustain large volume (~1 m$^3$), relatively cold (T<2000 K) diffuse plasmas in atmospheric air, with electron density up to ne-1013 cm$^{-3}$. For these applications, a power budget of the order of 1-10 MW/m$^3$ is desired. Finally, these plasma conditions are to be maintained for relatively long times, at least for 10 msec.

These goals define a highly nonequilibrium molecular plasma. The simultaneous requirement of electron densities of 1013 cm$^{-3}$ and gas temperatures at or below 2000 K represent an enormous departure from thermodynamic equilibrium, and rule out the use of purely thermal plasmas, such as high temperature arc discharges, to achieve this result.

Electron beams are identified as having by far the lowest power budget among all nonequilibrium ionization methods. Further, reliance on an external ionization source mitigates another principal difficulty known to exist in high-pressure discharges at large current densities, the well-known glow-to-arc transition, with subsequent plasma thermalization.

Even using an efficient ionization source the power budget required to sustain a relatively cold air plasmas is huge (>1 GW/m$^3$). This is predominantly due to rapid attachment of electrons to oxygen molecules. Consequently, reduction of the air plasma power budget mandates mitigation of electron attachment and, for further power reduction, lowering of the electron-ion recombination rate.

Experimental

Fig. 1 shows a schematic of the experimental setup. An electron gun generates an electron beam with an energy of up to 80 keV and a beam current of up to 20 mA. Pulsed operation of the electron gun at a low duty cycle prevents overheating and failure of the beam window separating the electron gun from the air plasma cell. A slow gas flow is maintained in the cell to provide flow convective cooling and to remove chemical products. Perpendicular to the e-beam axis a CO laser beam can be directed into the e-beam excited plasma. The laser is used to vibrationally excite the diatomic plasma constituents. The electron density in the e-beam sustained plasma is measured by microwave attenuation. The microwave measurement apparatus consists of a v=40 GHz oscillator, a transmitting and receiving antenna and waveguide system, oriented perpendicular to the e-beam and laser, and a transmitted microwave power detector.

With laser excitation, the lower($\leq10^9$) vibrational levels of CO, seeded into the gas mixture, are populated by direct resonance absorption of the CO laser radiation in combination with the much more rapid redistribution of population by the intramode vibration-to-vibration (V-V) exchange processes, These V-V processes then continue to populate the higher vibrational levels of CO above v=10, which arc not directly coupled to the laser radiation. At the same time, intermode V-V exchange processes, populate the vibrational levels of nitrogen and, due to the smaller vibrational quanta, preferentially vibrational levels of oxygen molecules. Therefore, in the laser-excited region, the concentrations of the vibrationally excited CO, O$_2$, and N$_2$ molecules are very high. Indeed, our previous experiments in high-pressure optically pumped plasmas [Plo06, Lei01, Lem90] showed that in atmospheric pressure air seeded with 4% CO, a 10 W CO laser can sustain fairly high vibrational temperatures of all three major diatomic species, $T_{v(CO)}$=2700 K, $T_{v(O_2)}=T_{v(N_2)}$=1900 K, while keeping the temperature low.

Results and discussion

The experimental results are compared with a kinetic model of the electron production, electron removal, and charge transfer processes in the investigated air plasmas. The model takes into account rates for electron production by the e-beam, electron-ion recombination, 3-body ion-ion recombination, electron attachment in 3-body collisions to O$_2$, and to N$_1$, electron detachment from O$_2$ in collisions with O$_2$ and in collisions with N$_2$. Electron densities, positive ion densities, and O$_2$ densities are calculated integrating the differential equations.

As mentioned before, the CO laser excited air plasma is in a very strong vibrational nonequilibrium. The vibrational temperature of the diatomic species exceeds the translational temperature by at least a factor of 4. Nevertheless, the fraction of molecules in excited vibrational states is still small compared to the population of the vibrational ground state. Therefore, the apparent complete mitigation of electron attachment to oxygen in vibrationally excited air cannot be caused by a vibrationally induced modification of the attachment rate itself because the ground-state O$_2$ molecules ($>50\%$) would still be exhibiting the full attachment rate, i.e. the total attachment rate could only be reduced by less than 50%. Consequently, the vibrational excitation has to be acting on the electron detachment side.

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The overall influence of these effects on the plasma power budget can be estimated as follows. In cold air plasmas the dominant
electron removal process is attachment to oxygen. The minimum power budget (assuming 100% ionization efficiency) to sustain a cold air plasma with an electron density of \(n_e=10^{14} \text{cm}^{-3}\) is therefore given by \(P_r=1.4 \times 10^6 \text{W/cm}^3\). For an average ionization energy in air of \(E_{\text{i}}=14 \text{eV}\) this gives \(P_r=1.4 \text{W/cm}^3=1.4 \text{GW/m}^3\). In the case of vibrationally excited air, the electron loss by attachment is replenished by detachment of electrons from \(O_2\) instead of \(O_3\) in the case of cold air. With an electron affinity of \(E_{\text{a}}=0.4 \text{eV}\) the minimum power budget to overcome attachment decreases to \(P_r=1.4 \times 10^6 \text{W/cm}^3\) at \(T=300 \text{ K}\) or \(P_r=10^6 \text{W/cm}^3\) at the reduced gas density at \(T=500 \text{ K}\). In case of mitigated attachment the main electron removal process in an electron beam sustained air plasma is dissociative electron-ion recombination. The minimum power budget to overcome recombination is given by \(P_r=1.4 \times 10^6 \text{W/cm}^3\). With an electron-ion recombination rate of \(\beta=1 \times 10^{-10} \text{cm}^3/\text{s}\), we obtain \(P_r=2.25 \times 10^6 \text{W/cm}^3\). With the measured recombination rate in vibrationally excited air, \(\beta=2 \times 10^{-10} \text{cm}^3/\text{s}\), the minimum power budget to overcome recombination decreases to \(P_r=4.5 \times 10^5 \text{W/cm}^3\). This, of course, does not yet include the efficiency of the laser excitation process and the efficiency of the electron beam ionization process.

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**References**


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**Figures**

Figure 1. Schematic of the plasma cell

Figure 2. Measured electron density pulse in 1 atm of vibrationally excited air compared with calculated electron density in \(N_2\). In strong contrast to a plasma in cold equilibrium air (dashed line) vibrationally excited air does not seem to exhibit any electron attachment to \(O_2\), i.e. peak electron density and plasma decay in vibrationally excited air seem to be purely caused by electron-ion recombination.

Figure 3. Experimental and calculated electron densities using increased electron detachment rates. Increase of the detachment rates by 5 orders of magnitude fully mitigates the effect of attachment and the calculated trace for laser excited air practically coincides with the calculated trace for \(N_2\).
Non-equilibrium state-to-state vibrational-chemical kinetics of diatomic gas flows

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Introduction

Non-equilibrium state-to-state vibrational-chemical kinetics of diatomic molecules is widely discussed in the recent papers on molecular lasers, atmosphere chemistry and various gas dynamic applications. A short review of the results obtained for different flows by means of solution of master equations for the vibrational level populations together with conservation equations is given, for instance in [1, 2].

An extension of the state-to-state model which permits to treat properly radiative transitions is of importance for laser technology, photochemistry, shock tube measurements as well as for estimation of the heat transfer caused by radiation.

A self-consistent model which allows to describe non-equilibrium gas mixture flows with coupled vibrational relaxation, chemical reactions, absorption and emission of photons based on the rigorous kinetic theory is proposed in [1]. This approach has been elaborated for the conditions when excitation of electronic molecular states can be neglected, i.e. for moderate gas temperature find high enthalpy flows.

Here the state-to-state model given in [1] is generalized by including in the kinetic scheme the vibrational-electronic (VE) transition and emission from the electronically excited state. As in one, the approach is based on the assumption of rapid equilibration of translational and rotational modes compared to the remaining processes. In this case the distribution over velocities and rotational energies follow the Maxwell-Boltzmann form, while no quasi- stationary distribution over vibrational energies (Boltzmann or Treanor) is established in the system. A closed set of macroscopic equations taking into account coupled vibrational and electronic relaxation, chemical reactions and radiative transitions is derived in [3]. The generalised Chapman-Enskog method allows one to derive a closed system of equations for the macroscopic parameters [1-4]. This system consists of the master equation for level vibrational populations, conservation of momentum and total energy and equation of radiative transfer [1].

Non-equilibrium CO kinetics

The kinetic model presented above can be applied for the investigation of any flow of diatomic neutral gas mixture. A molecule of carbon monoxide is chosen because of its importance for many applications: molecular lasers, environmental problem, planetary atmospheres exploration. CO kinetics has been widely discussed in the literature for many years, the peculiarities of shocked-heated CO flows have been studied experimentally in [5-6], the kinetics of electrical discharges and optically pumped CO remains the focus of attention for the last two decades [7-15].

The aim of this section is to give a short summary of recent results in this field and to list the main processes which have to be taken into account for the simulation of CO flow using the model described above.

Two kinds of radiative transitions are considered: (1) IR radiation due to the transitions between vibrational states and, (2) UV and visible caused by the transitions between electronic states.

Among the vibrational energy transfers we distinguish the VV exchange between the same electronic state, and using the formulas given in [12] for the transitions between electronic states.

The most intensive bands observed in the UV and the visible range are: CO fourth positive band (the responsible transitions are A1Π → X1Σg), CO Cameron band (a2Π → X1Σg) which is about 103 times less intensive than the fourth positive one [5]. Actually, several additional bands can be detected in the system (like CO third positive, C2 Doublon, Fox-Herzberg and Mulliken, and some O2 bands) but they appear to be rather weak [14].

Finally, we take into account only two electronically excited states: the lowest singlet and triplet CO states CO(a1Π) and CO(A1Π). The production terms due to radiation can be calculated using the Einstein coefficients [16] for the radiative transitions between vibrational levels within the same electronic state, and using the formulas given in [12] for the transitions between electronic states.

Among the vibrational energy transfers we distinguish the VV exchange between the same molecule:

\[ CO(v) + CO(w) \rightarrow CO(v') + CO(w') \]  (1)

and VT transfer,

\[ CO(v) + O_2(0) \rightarrow CO(v-1) + O_2(1) \]  (2)

and symmetric one-by-two quanta near-resonance VV exchange [15]

\[ CO(v) + CO(0) \rightarrow CO(v-2) + CO(1) \]  (3)

The state-specific rate coefficients for processes(1)-(4) are given by [12, 18-20]. One should mention that processes (2) and (3) involving transitions between highly excited states do not contribute significantly to the formation of vibrational distributions in shock-heated CO. However, they can influence noticeably the level populations in optically pumped systems and expanding flows with high storage of vibrational energy.

In VV pumped systems the VE transitions from high vibrational levels to the approxi- mately isoenergetic excited electronic states are found to be important [11-12][14-15]:

\[ CO(X^1Σ_u, v \sim 27) + M \rightarrow CO(A^3Σ_g, v \sim 0) + M \]  (5)

and,

\[ CO(X^1Σ_u, v \sim 40) + M \rightarrow CO(A^3Σ_g, v \sim 0) + M \]  (6)

In particular, transition (6) is the main reason for the persistent termination of the VE up-pumping to the levels above \( v \sim 40 \) observed in many experiments. On the contrary process (5) does not stop the VV up-pump. Nevertheless, perturbation of the ground electronic state vibrational populations due to this transfer has been observed by Farrenq [11].

We consider only the chemical dissociation of CO:

\[ CO + M \rightarrow C + O + M \]  (7)

and,

\[ O_2 + M \rightarrow 2O + M \]  (9)

they contribute very weakly in the CO kinetics in shock tube experiments as well as in the CO kinetics in shock tube experiments as well as in the VV pumped systems. However, the role of these processes is important in discharges [8].

Some carbon line radiation has also been observed [5,14] in both low and high temperature conditions.

The kinetics model presented above has been applied for the investigation of non-equilibrium CO flow behind a plane shock wave. The free-stream conditions are the following:

\[ a ]
The initial vibrational distributions of CO molecules are supposed to be in equilibrium at temperature T_0. Conservation equations have been solved in the stationary one-dimensional Euler approximation. VV (1), VT (4), VE (5)(6), exchanges as well as dissociation-recombination reaction (7) and radiative transitions have been taken into account for the simulation of production terms in the master equations.

The mass fraction of atoms and electronic states are rather low, the influence of electronic excitation on the total radiation intensity is found to be large. This is not the reason for a weak contribution of UV radiation to the total radiation intensity. It can be seen from Fig 2, where a comparison of total IR radiation intensity and intensities of UV radiation from the electronic state is presented. At higher temperature conditions the role of electronic states in radiative is expected to be more important.

The kinetic model of a non-equilibrium gas mixture with coupled VV, VT, VE exchanges, radiatives transitions and chemical reactions is presented. The flow of CO behind a shock wave is studied using state-to-state approach. Although the concentration of excited electronic states are rather low, the influence of electronic excitation on the total radiation intensity is found to be large under the conditions considered here.

**References**
