

STRONG DEPENDENCE OF ELECTRON KINETICS IN COLLISION DOMINATED He-CO rf PLASMA ON DIFFERENT ADMIXTURES OF CO¹⁾

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Electron energy distribution functions and mean collision frequencies for the uniform bulk plasma of established rf discharges in He/CO have been obtained by solving the time dependent Boltzmann equation. The results, which are of importance for plasma processing and laser technology, show that already small CO admixtures to He remarkably change the periodic behaviour of the energy distribution of the electrons by a drastic enhancement of the collisional energy dissipation effectiveness in the mixture. These changes can be interpreted on the basis of a lumped energy dissipation frequency in all electron collisions, which is determined by the atomic data of the electron collision processes as well as by the admixture fractions and which drastically increases with an increasing CO admixture.

1. INTRODUCTION

The modelling of strongly time dependent plasmas (radio frequency, microwave, pulse-like ones) used for plasma technology (etching, deposition, laser medium) has clearly indicated the large importance of a detailed knowledge of the non-stationary electron velocity distribution function, in particular of the isotropic part of the latter, and of the resultant mean collision frequencies for the main electron impact reactions as excitation, dissociation and ionization of a particular feed gas [1], [2].

By an exact solution of the time dependent, spatially uniform Boltzmann equation, the isotropic distribution (ID) in the bulk of rf discharges in inert and molecular gases has been comprehensively studied [3—6].

However, in application to plasma technology one uses discharges in mixtures containing often only a small admixture of a molecular component to an

¹⁾ Contribution presented at the 7th Symposium on Elementary Processes and Chemical Reactions in Low Temperature Plasma, STARÁ TURÁ-DUBNÍK, June 13—17, 1988

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inert gas. This paper reports isotropic distributions and relevant macroscopic quantities for the bulk plasma of an rf discharge in He/CO mixtures in comparison with the corresponding quantities relevant to pure He and CO.

II. BOLTZMANN EQUATION AND LUMPED DISSIPATION FREQUENCIES OF A MIXTURE PLASMA

The basic equation for the He/CO mixture is the non-stationary, spatially uniform Boltzmann equation for the electron velocity distribution $F(\vec{v}, t)$

$$\frac{\partial F}{\partial t} - \frac{e_u}{m} \cdot \frac{\partial F}{\partial \vec{v}} = \sum_j \left(C_j^d + \sum_k C_{j,k}^m \right) \quad (1)$$

in the rf field

$$\vec{E} = E_{\vec{e}}, \quad E(t) = E_0 \cos(\omega t). \quad (2)$$

In (1) the index j refers to the component j , i.e. to He and CO, respectively and the meaning of the other symbols is the usual one [4].

The Legendre polynomial expansion of $F(\vec{v}, t)$ in (1) gives in the Lorentz approximation finally two partial differential equations for the isotropic part and for the first contribution to the anisotropic part of $F(\vec{v}, t)$, generalized for a mixture plasma.

As already it has been successfully done for rf plasmas in pure gases [4], the results for the mixture will be interpreted in terms of two normalized lumped frequencies for the energy and the impulse dissipation in all electron collisions. For the generalized case of a mixture they are given by

$$\begin{aligned} \frac{\nu_e(U)}{p_0} &= \sum_j \frac{N_j}{N} \left(2 \frac{m}{M_j} \frac{\nu_{j,d}(U)}{p_{0,j}} + \sum_k \frac{\nu_{j,k}^m(U)}{p_{0,j}} \right) = \sum_j \frac{N_j}{N} \left(\frac{\nu_e(U)}{p_0} \right)_j \\ \frac{\nu_e(U)}{p_0} &= \sum_j \frac{N_j}{N} \left(\frac{\nu_{j,d}(U)}{p_{0,j}} + \sum_k \frac{\nu_{j,k}^m(U)}{p_{0,j}} \right) = \sum_j \frac{N_j}{N} \left(\frac{\nu_e(U)}{p_0} \right)_j. \end{aligned} \quad (3)$$

In these relations again the index j refers to the two components and $\nu_{j,d}$ and $\nu_{j,k}^m$ represent the collision frequency for the impulse transfer in elastic collisions and for the k th inelastic collision process with the component j , which are dependent on the electron energy.

For example $\nu_{j,k}^m = v N_j Q_{j,k}^m(v)$, where N_j is the density of the gas component j and $Q_{j,k}^m(v)$ the total cross section for the k th inelastic collision process of the electrons with molecules of the component j . U means the instantaneous electron energy in eV ($e_0 U = mv^2/2$) and

$$p_0 = \sum_j p_{0,j}, \quad p_{0,j} = N_j/n_e, \quad N = p_0 n_e \quad (n_e = 3.54 \times 10^{16} \text{ cm}^{-3} \text{ Torr}^{-1})$$

denote the total gas pressure of the mixture, the partial pressures of the components (all at 0°C) and the total gas density. Due to the normalization of ν_e and ν_e on p_0 the dissipation frequencies ν_e/p_0 and ν_e/p_0 are determined by the different collision cross sections, the ratios m/M_j of the electron mass to the gas particle mass and the admixture fractions N_j/N of the components, i.e. only by the atomic data of the collision processes and the admixture fractions.

Both these lumped dissipation frequencies describe the effectiveness of the energy and impulse dissipation of the electrons in their energy space by all collision processes. Thus the rapidity of the alteration of the rf field, which is characterized by the normalized field frequency ω/p_0 , determines in relation to both normalized lumped dissipation frequencies the degree of modulation and the corresponding phase shift of the ID with respect to the rf field and of the relevant macroscopic quantities [4], [5].

Especially for $\omega/p_0 \ll \nu_e/p_0$ a quasistationary behaviour of the ID with a very large modulation occurs, whilst for the reverse relation $\omega/p_0 \gg \nu_e/p_0$ the ID becomes practically time independent.

III. RESULTS AND INTERPRETATION

The partial differential equations resulting from the Legendre polynomial expansion of (1) have been solved numerically up to the establishing of the periodic state by applying the collision cross sections of CO used in [5] and of He used in [7]. The calculations of ID and the relevant macroscopic quantities

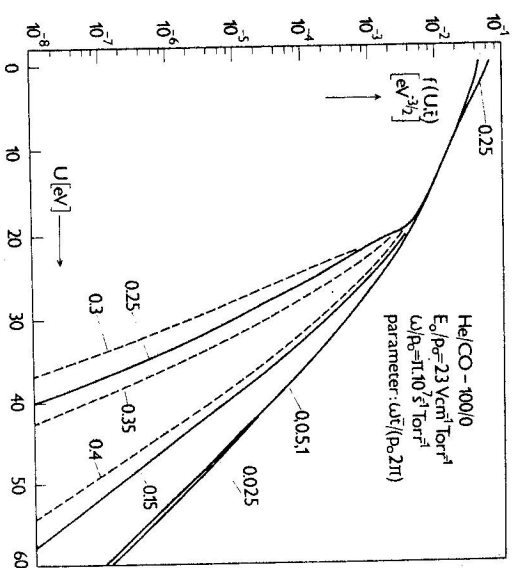


Fig. 1. Periodic behaviour of ID at $E_0/p_0 = 23 \text{ V cm}^{-1} \text{ Torr}^{-1}$ for pure He.

have been performed for a normalized field frequency value of $\omega/p_0 = \pi \times 10^3 \text{ s}^{-1} \text{ Torr}^{-1}$ relevant to the rf discharge plasmas in the MHz region. Now we discuss the periodic behaviour of ID for a relatively large field amplitude of $E_0/p_0 = 23 \text{ V cm}^{-1} \text{ Torr}^{-1}$, which is more typical of the rf plasma processing. As in the case of the one component rf discharge plasma a normalized time scale $\bar{t} = p_0 t$ can be introduced also in a mixture.

Fig. 1 shows the periodic evolution of ID in pure He with $\omega/(p_0 2\pi) = 1/T$ (T being the period of the rf field) as a parameter of the curves. The corresponding energy distribution of the electrons is directly obtained by ID, i.e. by the multiplication of ID with the square root $U^{1/2}$ of the electron energy. As obvious the modulation of the ID is almost absent in the region of the low energies up to 20 eV, while a remarkable modulation is present in the region of the electronic excitation and the ionization of He.

Fig. 2 reports ID's periodic behaviour for a mixture containing 10% CO. Now, a remarkable modulation occurs also at lower energies despite the small admixture fraction of only 10%. Moreover the ID is on the period average much more depopulated at higher electron energies.

Finally Fig. 3 shows the periodic behaviour of ID in the limiting case of pure CO. Now, extremely large modulations of ID occur at energies around 2 eV and above 6 eV and large temporal alteration in the intermediate range.

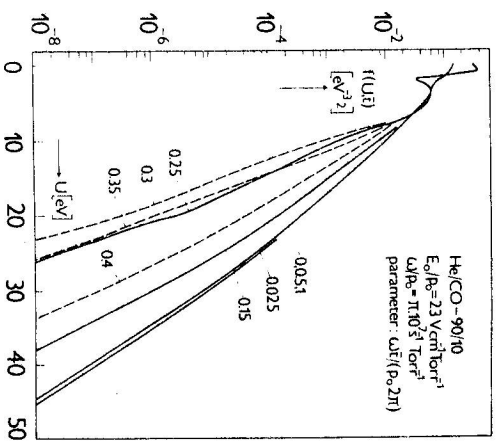


Fig. 2. Periodic behaviour of ID at 10% CO admixture.

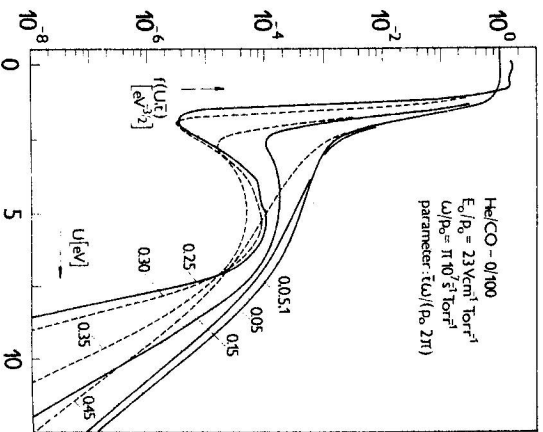
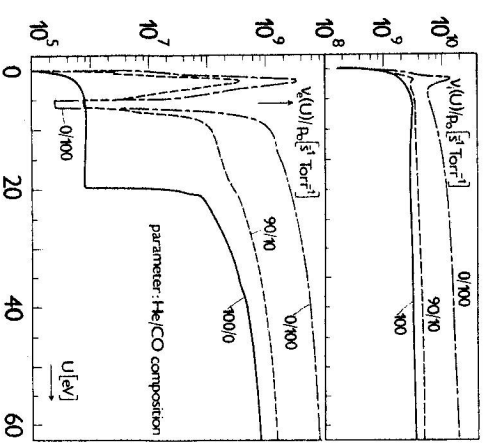


Fig. 3. Periodic behaviour of ID for pure CO.

These figures clearly indicate a very strong change of ID's periodical behaviour at the fixed field frequency ω/p_0 and the field amplitude E_0/p_0 when passing from an rf plasma in pure He via the He/CO mixtures to pure CO. This behaviour can be microphysically interpreted on the basis of the relation of the field frequency ω/p_0 to the lumped energy dissipation frequency ν_i/p_0 . To that end Fig. 4 reports the normalized lumped frequencies for impulse and energy dissipation for pure He, for a He/CO mixture with 10% CO admixture and for pure CO. In pure He large values of the lumped energy dissipation frequency only occur in the energy region of intense electronic excitation, i.e. above 20 eV.

Fig. 4. Normalized lumped frequencies $\nu_i(U)/p_0$ and $\nu_e(U)/p_0$ for impulse and energy dissipation as dependent on the electron energy.



The presence of a small CO admixture considerably increases the lumped energy dissipation frequency ν_e/p_0 , mainly in the energy region of 0–20 eV. In particular, the strong peak at about 2 eV in ν_e/p_0 is due to an intense vibrational excitation in CO, and the large enhancement in ν_i/p_0 above 6 eV, especially between 6 and 20 eV is due to a large electronic excitation, dissociation and ionization in CO. In addition Fig. 4 shows a further pronounced increase of the normalized energy dissipation frequency when going from a 10% CO admixture to the pure CO case due to the very different magnitude of the collision cross sections in He and CO and therefore of the lumped energy dissipation frequency relevant to these pure gases. As a consequence of this large change in the lumped energy dissipation frequency with the CO admixture we have at not too large field frequencies ω/p_0 (i.e. at $\pi \times 10^3$ considered) in pure He large modulation of ID only in the high energy region, i.e. above 20 eV. For energies below the threshold the lumped energy dissipation frequency for inelastic collision

processes in He (19.5 eV) is much smaller than the considered field frequency ω/p_0 , while the reverse is true above the threshold. Thus a rapid collisional energy dissipation at higher energies due to the excitation and the ionization of the atoms occurs, however, is no longer possible at lower energies. For a 10% CO admixture v_e/p_0 becomes for energies around 2 eV and above 6 eV already remarkably larger than the considered field frequency ω/p_0 so that there still occurs a rapid collisional energy dissipation in these energy regions, which leads to the observed large modulation and the depopulation of the ID on the period average at higher electron energies. Finally, for pure CO the just mentioned effects on the ID are, of course, still much more pronounced.

ID's so far reported, have a large portion of electrons with relatively high energies. Generally for laser applications one requires mainly electrons at lower energies (of a few eV), so that one must consider rf plasmas with lower rf field amplitudes.

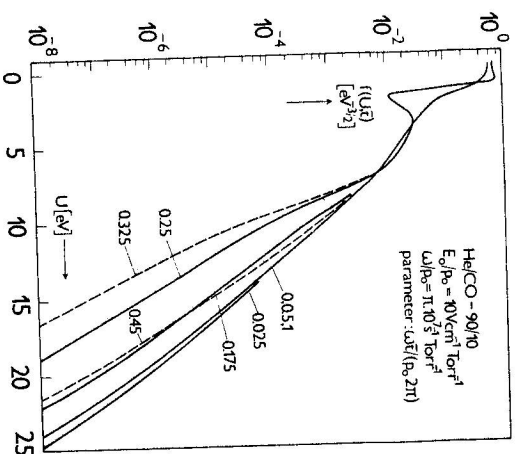


Fig. 5. Periodic behaviour of ID at $E_0/p_0 = 10 \text{ V cm}^{-1} \text{ Torr}^{-1}$ and at 10% CO admixture.

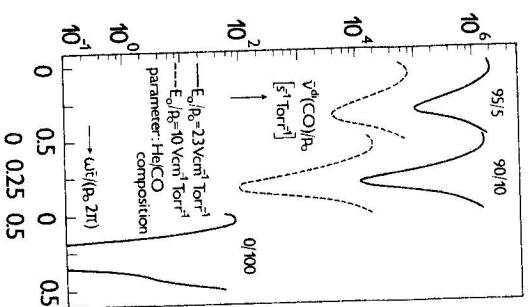


Fig. 6. Periodic behaviour of the mean collision frequency $v^m(\text{CO})/p_0$ for dissociation of CO at the two field strength values considered.

Therefore, Fig. 5 reports for a 10% CO admixture the periodic evolution of ID at the same field frequency, however, at the smaller field amplitude of $10 \text{ V cm}^{-1} \text{ Torr}^{-1}$. As one can appreciate, at the smaller rf electric field a similar periodic behaviour of ID with a large modulation is obtained, as in

Fig. 2. Thus for such a decreased E_0/p_0 the same interpretation of this behaviour by means of the lumped energy dissipation frequency can be used.

The great impact of different CO admixtures on the periodic behaviours of ID's is also reflected in the periodic behaviour of relevant mean collision frequencies for the different inelastic electron collision processes with the mixture components. To give at least one example, Fig. 6 reports for two field strengths with an increasing CO admixture the mean collision frequency $v^m(\text{CO})/p_0$ for the dissociation of the CO molecules with a threshold energy of 11.09 eV. A monotone decrease of this collision frequency occurs with growing CO admixture despite that this mean collision frequency increases proportionally to the CO admixture fraction.

Furthermore, a remarkable increase of the modulation of this quantity with the growing CO admixture results due to the correspondingly larger modulation of ID at higher energies.

Concluding we would like to emphasize that a sensitive alteration of the periodic behaviour of the ID and of the resultant mean collision frequencies in the established rf plasma results when passing, at an uncharged field amplitude E_0/p_0 and field frequency ω/p_0 , from an rf plasma in pure He to He/CO mixture plasmas with an increasing CO admixture. This sensitivity is mainly caused by the drastic change of the collisional energy dissipation effectiveness of pure He when adding CO, already at very small CO admixtures. This sensitive dependence must be taken into account when modelling such mixture plasmas.

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Received July 13th, 1988

Accepted for publication September 27th, 1988

СИЛЬНАЯ ЗАВИСИМОСТЬ КИНЕТИКИ ЭЛЕКТРОНОВ В Ne-CO ПЛАЗМЕ С ДОМИНИРУЮЩИМИ СОУДАРЕНИЯМИ ОТ РАЗЛИЧНЫХ ПРИМЕСЕЙ

Функции распределения энергии электрона и средняя частота соударений для различного объема плазмы установленных t_f разрядов в Ne/CO были получены решением зависящего от времени уравнения Больцмана. Результаты, которые играют важную роль в плазменной обработке и лазерной технологии, показывают, что даже малейшая добавка CO в Ne существенно меняет периодическое поведение распределения энергии электронов, сильно увеличивая эффективность диссипации энергии соударений в смеси. Эти изменения можно объяснить на основе частоты диссипации общей энергии во всех электронных соударениях, которая определяется как атомными данными для процессов столкновений электронов, так и долями примесей, и которая существенно увеличивается с увеличением примеси CO .