Non L.T.E. Properties of Quasistationary Oxygen Plasmas

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The non L.T.E. (local thermodynamic equilibrium) properties of optically thin and thick quasistationary oxygen plasmas have been calculated for the temperature range $kT=0.5-1.5$ eV and for the electron density interval 10^8-10^{16} cm^{-3}, by using the collisional-radiative model of Bates, Kingston and McWhirther. The results include [1] the coefficients $r_0(i)$ and $r_1(i)$, which represent the contribution to the population density of the ith quantum level from the continuum and from the ground state, respectively [2] the values of α and S, which are the collisional-radiative recombination and ionization coefficients, respectively. The accuracy of the present results is discussed in connection with the adopted plasma model and with the selection of the collisional cross sections for forbidden and allowed transitions. A discussion is also presented of the influence of the two low lying excited states of oxygen atoms (i.e. the states $2p^4\,{}^1D$, $2p^4\,{}^1S$) on the non L.T.E. properties of these plasmas. A satisfactory agreement is found with the calculations of Julienne et al. and with the experimental results of Jones.

I. Introduction

The equilibrium properties of atomic oxygen and nitrogen plasmas have been extensively studied for a large range of temperature and pressure [1]. Less work exists on the non L.T.E. properties of these plasmas, despite the fact that in many laboratory conditions the plasma is far from L.T.E. conditions. Park considered collision dominated nitrogen plasmas, in which the ground state density was taken as an independent parameter, while Catherinot and Sy [3] recently extended Park's calculations including diffusion effects. Oxygen plasmas have been treated in the cascading radiative model by Julienne et al. [4] and some of these authors [5] extended the calculations to include the collisional processes, limiting however their study to recombining plasmas. Their results apply specially when excitation from the ground state can be neglected ($kT_e \leqq 0.5$ eV). More recently Cacciatore and Capitelli [6] studied the transient behaviour of oxygen plasmas, pointing out the importance of the metastable $3s^5S$ state in affecting the temporal evolution of the population densities of the excited states.

In this work we examine the behaviour of quasistationary oxygen plasmas, i. e. of plasmas for which the temporal derivatives of the population densities of the excited states can be neglected compared to that of the ground state. These conditions allow the definition of the so called collisional radiative recombination (α) and ionization (S) coefficients, which are indeed of great importance for a prediction of the evolution of the electron density in a plasma. The results, which refer to electron densities ranging from 10^8 to 10^{16} cm^{-3} and to electron temperatures $kT=0.5-1.5$ eV, will be discussed in connection with the adopted plasma model and with a selection of the cross sections for allowed and forbidden collisions. Moreover the influence of the two low lying excited atomic oxygen states (i. e. $2p^4\,{}^1D$, $2p^4\,{}^1S$) on the α and S coefficients will be examined.

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2. Non L.T.E. Oxygen Plasmas

The non L.T.E. properties of optically thick atomic oxygen plasmas [$O(i)$, $O^+(^4S)$ and electron e] can be deduced from a system of coupled differential equations of the type [7]

$$\begin{aligned}\partial n_i/\partial t = {} & n_e \sum_{j \neq i} n_j K_{ji} + n_e^2 n_+ K_{ci} \\ & - n_i n_e \Big(K_{ic} + \sum_{j\neq i} K_{ij}\Big) + n_e^2 \beta_i + \sum_{j>i} n_j A_{ji} \\ & + n_i \sum_{j<i} (1-\lambda_{ij}) A_{ij} - n_i \sum_{j<i} A_{ij} - n_e^2 (1-\lambda_i) \beta_i \\ & - \sum_{j>i} n_j (1-\lambda_{ji}) A_{ji} \qquad (1)\end{aligned}$$

$$-\partial n_e/\partial t = \sum_i \partial n_i/\partial t = \gamma(t)\, n_+ n_e \qquad (2)$$

where n_e, n_i and n_+ are the densities for the electron, the ith quantum level and the ions, respectively. Equation (1) refers to a homogeneous plasma, in which only radiative and electronic collisional processes are effective in populating and depopulating the levels. The rate coefficients of Eq. (1) correspond to the following microscopic processes

1) Collisional ionization and three body recombination

$$e + O(i) \underset{K_{ci}}{\overset{K_{ic}}{\rightleftharpoons}} e + O^{+} + e\,;$$

2) Collisional excitation and deexcitation

$$e + O(i) \underset{K_{ji}}{\overset{K_{ij}}{\rightleftharpoons}} e + O(j)\,;$$

3) Spontaneous emission and reabsorption

$$O(i) \underset{(1-\lambda_{ij})A_{ij}}{\overset{A_{ij}}{\rightleftharpoons}} O(j) + h\,v\,;$$

4) Radiative recombination and photoionization

$$O^{+}(^4S) + e \underset{(1-\lambda_i)\beta_i}{\overset{\beta_i}{\rightleftharpoons}} O(i) + h\,v\,.$$

The λ_{ij} and λ_i parameters are related to the processes of photo-absorption and photo-ionization, respectively, and they characterize the plasmas as optically thin for $\lambda_{ij} = \lambda_i = 1$ and optically thick for $0 \leqq \lambda_{ij}, \lambda_i < 1$ [8].

The plasma will be moreover defined as a recombining or an ionizing one depending on $\gamma(t) > 0\ (\partial n_e/\partial t < 0)$ or $\gamma(t) < 0\ (\partial n_e/\partial t > 0)$, respectively [7].

Solution of the system 1 – 2 can be obtained once the number of quantum levels belonging to the plasma has been defined. Figure 1 shows the schematic energy diagram of the levels utilized in these calculations. We have considered the two low lying excited levels $2p^4\,{}^1D$, $2p^4\,{}^1S$ and the ns^3S, ns^5S, np^3P, np^5P ... up to $n = 6$. Above this principal quantum number, the levels have been coalesced in different groups up to $n = 11$. Moreover we have also included the $3s'^3D^0$ and $3s'^1D^0$ states, which belong to a different configuration of the core electron.

Both the energies and the statistical weights have been taken from Moore's tables [9] with the missing energies estimated by extrapolation techniques. The collisional rate coefficients appearing in Eq. (1) have been obtained by means of Gryzinski's theory for allowed and forbidden transitions [10, 11], while the radiative coefficients have been taken from different sources (see Reference [6]). The radiative recombination rates β_i for $kT = 0.5 - 1.5$ eV have been obtained scaling the 1 eV values with a $T^{-3/2}$ law.

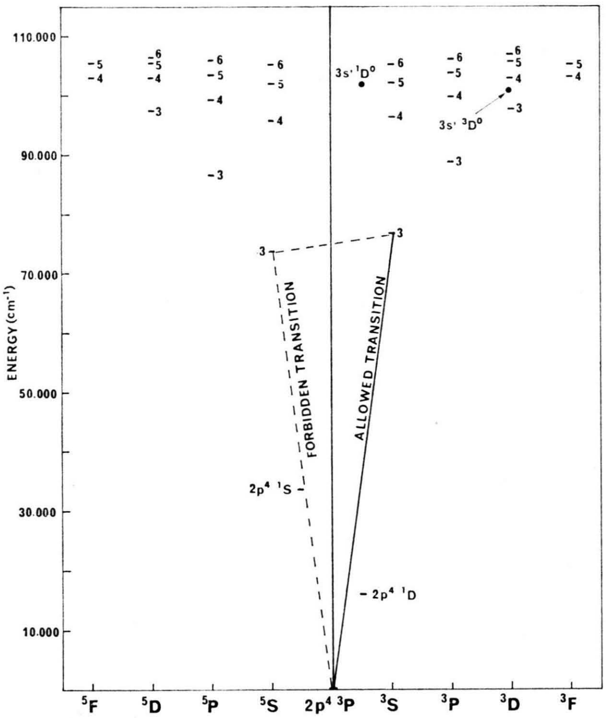

Fig. 1. Schematic energy diagram used in the present calculations. (The states with the angular momentum $L > 3$ and with the principal quantum number $n > 6$ have not been reported in the figure. The numbers in the figure indicate the principal quantum number.)

3. Quasistationary Oxygen Plasmas

Following Bates et al. [12] one can define a quasistationary state condition by equating to zero all master Eq. (1), but that relative to the ground state

$$\partial n_i/\partial t = 0 \quad \text{for} \quad i \geqq 2\,. \tag{3}$$

We then obtain a linear system of equations that can be solved taking the ground state (n_1) and the electron (n_e) densities as parameters.

The solutions are usually expressed by means of the $r_0(i)$ and $r_1(i)$ coefficients, which are related to Saha's decrements, b_i through

$$b_i = n_i/n_{iE} = r_0(i) + (n_1/n_{1E})\,r_1(i) \tag{4}$$

(subscript E refers to equilibrium conditions).

The coefficient $r_0(i)$ represents the contribution to the population of the ith level from the continuum of the free electrons, while $r_1(i)$ is the corresponding contribution by direct excitation from the ground state.

It is worth noticing that Eq. (3) considers the two low lying excited states $2p^4\,{}^1D$, $2p^4\,{}^1S$ (referred to later as levels 2 and 3 respectively) as the other excited states, despite the fact that their densities do not completely fulfil the condition

$$n_2, n_3 \ll n_1 \tag{5}$$

which is indeed at the basis of Equation (3). To overcome a similar difficulty for a nitrogen plasma, Park defined a quasistationary condition

$$\partial n_i/\partial t = 0 \quad \text{for} \quad i \geqq 4 \tag{6}$$

i. e. the low lying excited states of nitrogen are treated as the ground state. Condition 6 could be applied also to oxygen plasmas and the resultant system of equations then solved taking n_1, n_2, n_3 and n_e as parameters.

The definitions of quasistationary (QSS) plasmas by means of Eqs. (3), (6) apparently seem to be contradictory. To justify Eq. (3) for oxygen plasmas, it should be noted that the temporal derivatives of the states 2 and 3 are much smaller than the corresponding ground state values for a large interval of time[6], while Eq. (6) can be justified by the fact that the densities of levels 1, 2, 3 do not modify their values during the time in which the other excited states reach their QSS values[6]. Any way, a very good agreement is found between the values of $b_i (i \geqq 4)$ obtained by the two procedures, so that the use of condition (3) is completely satisfactory in the case of oxygen plasmas.

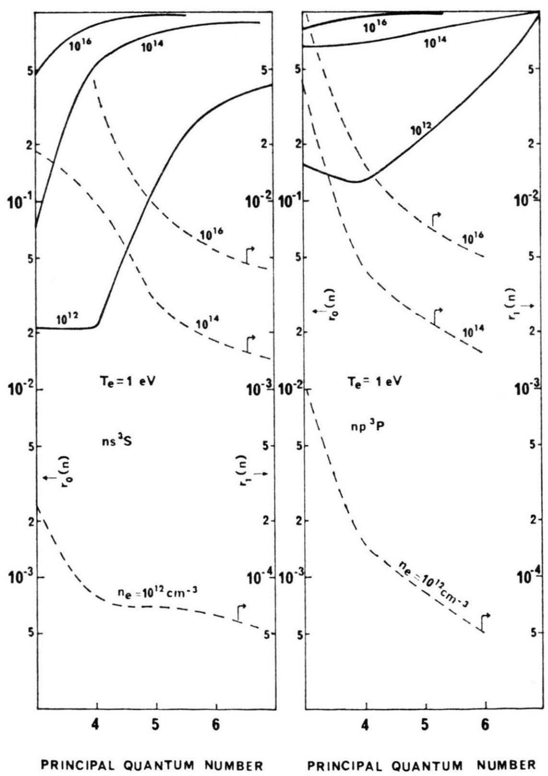

Fig. 2. Values of $r_0(n)$ (full lines) and $r_1(n)$ (dashed lines) as a function of the principal quantum number at different electron densities (cm^{-3}) for the series ns^3S and np^3S ($k\,T_e = 1$ eV, thin plasmas).

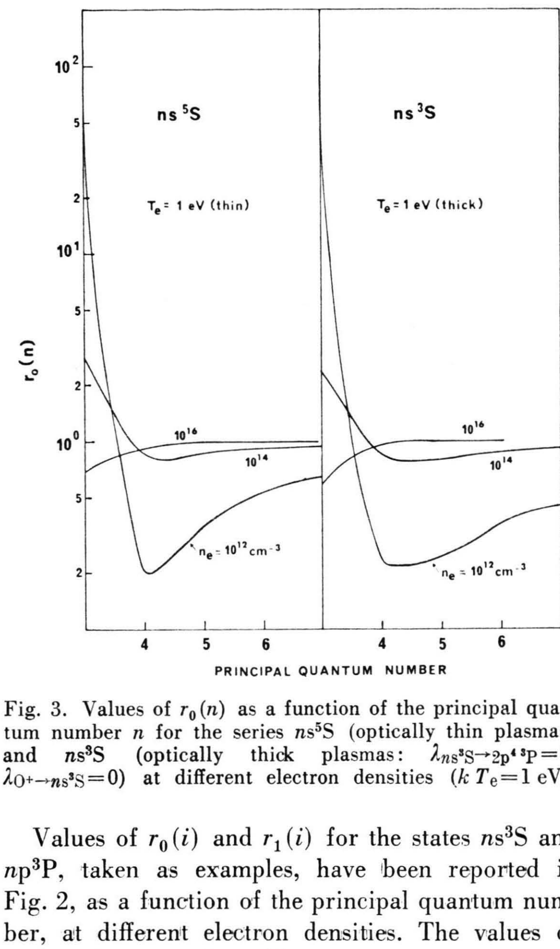

Fig. 3. Values of $r_0(n)$ as a function of the principal quantum number n for the series ns^5S (optically thin plasmas) and ns^3S (optically thick plasmas: $\lambda_{ns^3S \to 2p^4\,^3P} = 0$, $\lambda_{O^+ \to ns^3S} = 0$) at different electron densities ($k\,T_e = 1$ eV).

Values of $r_0(i)$ and $r_1(i)$ for the states ns^3S and np^3P, taken as examples, have been reported in Fig. 2, as a function of the principal quantum number, at different electron densities. The values of $r_0(i)$ relative to the ns^3S sequence are lower than the corresponding results for np^3P on account of the greater radiative rates of the ns^3S sequence. Figure 3 shows the behaviour of $r_0(i)$ for the ns^5S states indicating a strong overpopulation of the $3s^5S$ state at low $n_e{'}s$, since this level is not radiatively connected with the ground state. In Fig. 3 we have plotted $r_0(i)$ values for the ns^3S sequence in a thick plasma, in which complete reabsorption has been allowed for the transition $ns^3S - 2p^4\,^3P$ and for the continuum radiative recombination $O^+(^4S) - ns^3S$. It should be noted the similar behaviour of the ns^3S and ns^5S sequences, as a consequence of the radiative reabsorption along the ns^3S states.

4. Collisional Radiative Recombination and Ionization Coefficients

The $r_0(i)$ and $r_1(i)$ coefficients are useful for a computation of the collisional radiative recombination (α) and ionization (S) parameters. At the quasistationary conditions one can infact write

$$-\partial n_e/\partial t = \partial n_1/\partial t = \gamma\, n_+ n_e = (\alpha - S\, n_1/n_+)\, n_+ n_e \tag{7}$$

with α and S given by

$$\alpha = (n_{1E}/n_e^2)\,[-b_1 + \sum_{j>1} a_{1j}\, r_0(j)]\,, \tag{8}$$

$$S = (1/n_e)\,[-a_{11} - \sum_{j>i} a_{1j}\, r_1(j)]\,, \tag{9}$$

$$b_1 = -(n_e n_+/n_{1E})\,(\beta_1 + n_e K_{c1})\,, \tag{10}$$

$$a_{1j} = (n_{jE}/n_{1E})\,(A_{j1} + n_e K_{j1})\,, \tag{11}$$

$$a_{11} = -n_e (K_{1c} + \sum_{k>1} K_{1k})\,. \tag{12}$$

Values of α and S for optically thin and thick oxygen plasmas, at different temperatures, have been reported as a function of n_e in Figure 4. It should be interesting to know the time after which Eq. (7) can be utilized i. e. the time after which γ reaches its QSS value. In Fig. 5 we have reported the γ values obtained by solving the system of differential equations [6], together with the corresponding QSS value obtained in this work. One can note that the times necessary to achieve a QSS condition are of the order of 10^{-8} and 10^{-7} sec for $n_e = 10^{14}$ and 10^{12} cm^{-3} respectively.

The accuracy of the calculated α and S values relies on i) the adopted energy diagram ii) the role played by the forbidden transitions iii) the role of low lying excited states iiii) the choice of the collisional cross sections for the allowed transitions.

As for point i) we can say that a more complicated energy diagram could in principle be used, however errors in the corresponding cross sections would probable compensate for the improvement in the energy diagram. Moreover a recent study on quasistationary hydrogen plasmas in the same conditions of temperature and electron densities has shown that the principal quantum number 10 can

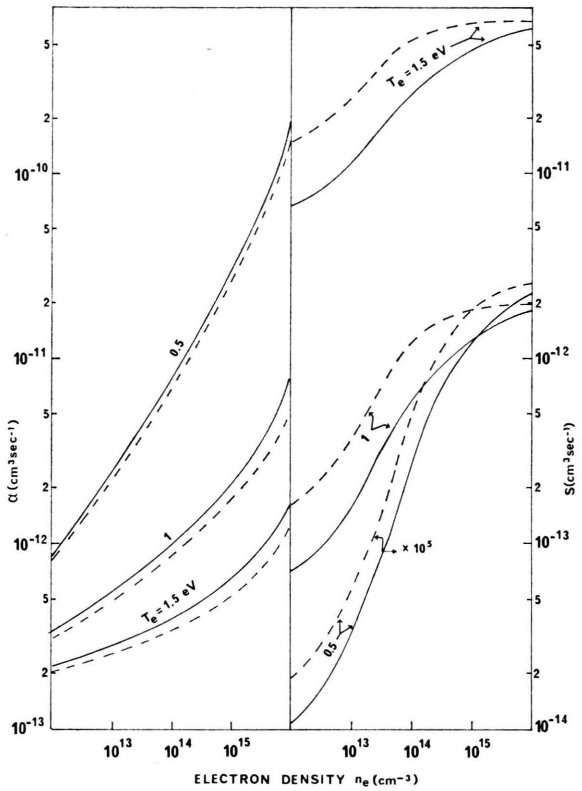

Fig. 4. Values of α and S as a function of the electron density at different temperatures for optically thin (full lines) and thick (dashed lines) oxygen plasmas (thick plasma as in Figure 3).

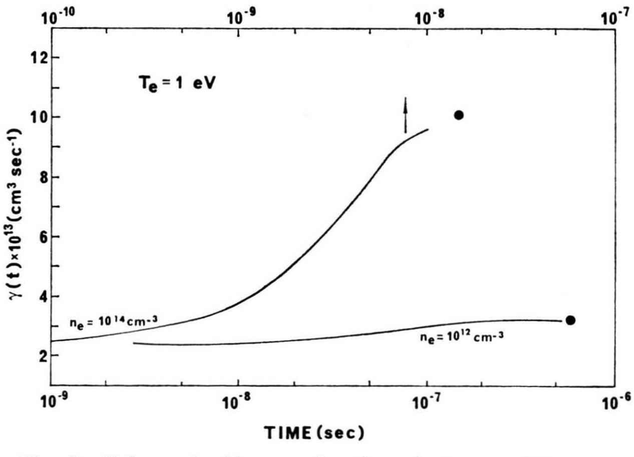

Fig. 5. Values of $\gamma(t)$ as a function of time at different electron densities [see Eq. (2) and Ref. 6]. ● Values of $\gamma = \alpha$ at the quasistationary conditions (optically thin plasmas, $k\,T_e = 1$ eV).

be considered as a practical cut-off level for truncating the system of linear equations [13].

In Fig. 6 a comparison is made between the values of α and S calculated with and without the collisional forbidden transitions. One can note that the neglection of the forbidden collisional transitions has a strong effect (up to a factor 4) on the collisional-radiative ionization coefficients S, while a minor influence (up to 50%) is found on the collisional-radiative recombination coefficient α. As for the role of levels 2 and 3, this can be deduced from Fig. 7, where the present α and S values are compared to those obtained by increasing the collisional rates from levels 2 and 3 by a factor of 4. One can note that differences up to 50% are obtained for the S coefficient, while a minor effect is found on α (up to 20%). The differences increase with increasing electron density.

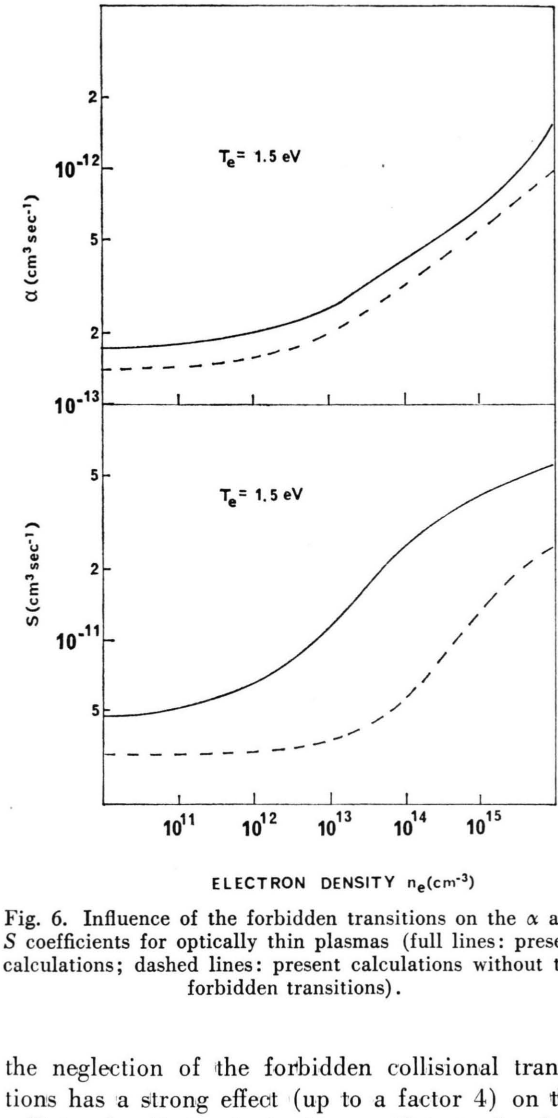

Fig. 6. Influence of the forbidden transitions on the α and S coefficients for optically thin plasmas (full lines: present calculations; dashed lines: present calculations without the forbidden transitions).

As for point iiii) we have recalculated the coefficients α and S using Drawin's cross sections [14] for the allowed collisional transitions and for the ionization. The use of these cross sections yields differences up to a factor of 2 for the S coefficient and up to 30% for α as compared to the present results (obtained with Gryzinski's formulas). It should be noted that Drawin's cross sections, based on a semiempirical approach, are close to the corresponding quantum mechanical formulation of Seaton [15], while Gryzinski's cross sections have been derived on the basis of semiclassical ideas.

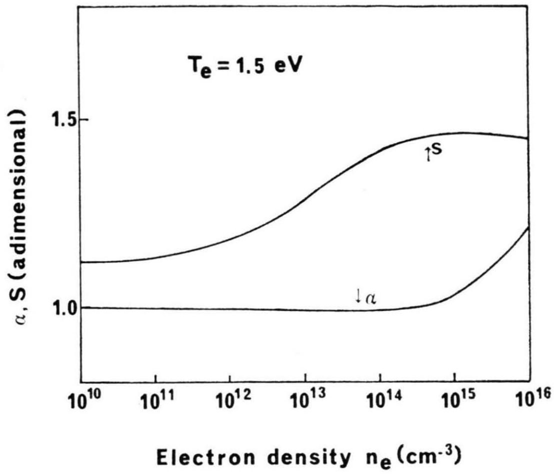

Fig. 7. Values of α and S coefficients as a function of the electron density normalized to the corresponding values obtained by increasing by a factor 4 the collisional rates from levels 2 and 3.

It is very difficult to choose between Gryzinski's and Drawin's formulas, since in some cases a theory agrees with the experimental cross sections better than the other one, while in other cases it happens the opposite [16].

A general property of the two formulas is their prediction of large cross sections for transitions corresponding to small energy gaps.

5. Comparison with Other Authors

It should interesting to compare the present results with those obtained by Julienne et al. [5] for recombining oxygen plasmas. These authors used a more complicated energy diagram (up to $n = 18$), neglecting, however, the two low lying excited states and the states $3s'^3D^0$ and $3s'^1D^0$. Moreover they used Drawin's cross sections for the ionization processes, Seaton's cross sections for collisional allowed transitions [15], while the cross sections for the forbidden transitions were empirically calculated scaling with an arbitrary factor the corresponding cross sections for allowed transitions.

Figures 8 – 9 show a comparison of the present b_i values [for recombining optically thin plasmas $b_i \cong r_0(i)$] with the corresponding values calculated by Julienne et al. and with the recent experimental determinations of Jones [17]. Our results seem to reproduce the experimental values better than the values of Julienne et al. The agreement (specially for $kT_e = 0.44$ eV, $n_e = 1.04 \cdot 10^{13}$ cm^{-3}) could be ascribed to the insertion in our model of the states $2p^4\,{}^1D$, $3s'\,{}^1D^0$, as emphasized recently by Jones.

The level $3s'\,{}^1D^0$, infact tends to depopulate the levels $4d^5D$, $3s^3S$ and $5s^5S$ populating by an optically radiative transition the level $2p^4\,{}^1D$.

Figure 10 gives a comparison of the present α values with those of Ref. [5], showing a satisfactory agreement in spite of the different methods used in the two calculations.

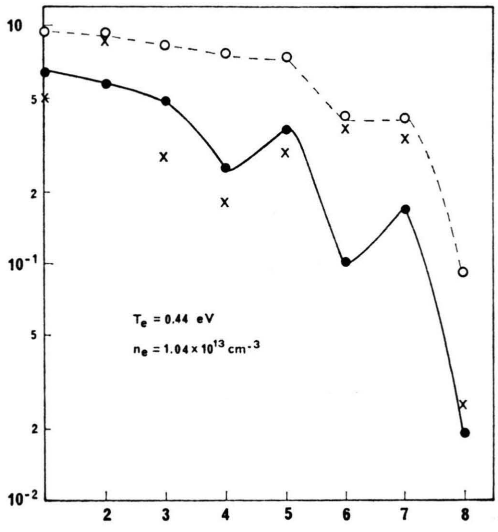

Fig. 8. A comparison of the present b_i values (●–●) with the calculations of Ref. 5 (○– –○– –○) and with the experimental values of Ref. 17 (×). (States: 1=$5d^5D$; 2=$6s^5S$; 3=$4d^5D$; 4=$5s^3S$; 5=$5s^5S$; 6=$4p^3P$; 7=$4p^5P$; 8=$3p^5P$.)

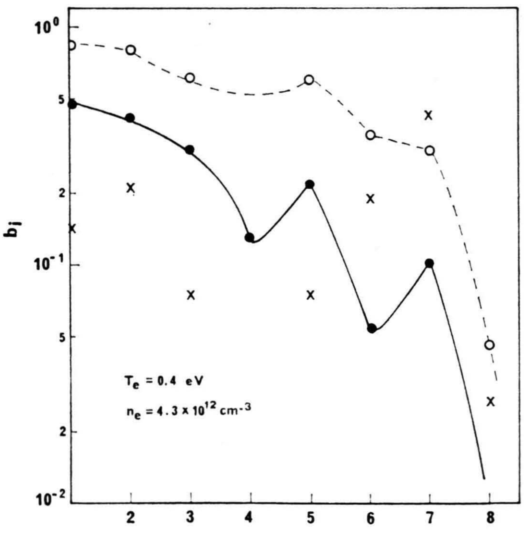

Fig. 9. A comparison of the present b_i values (●–●) with the calculations of Ref. 5 (○– –○– –○) and with the experimental values of Ref. 17 (×). (States: as in Figure 8.)

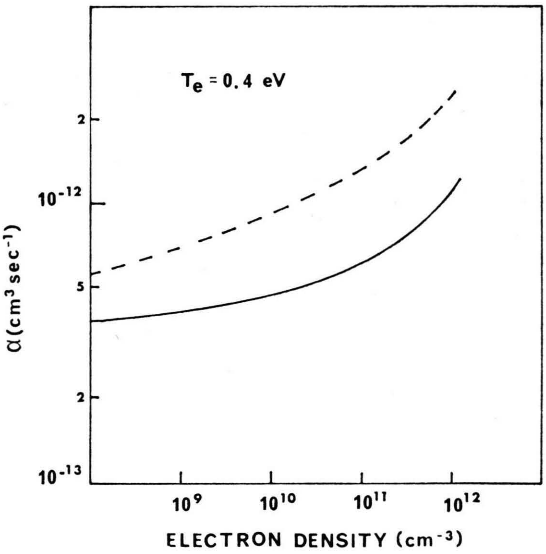

Fig. 10. A comparison of the present α values (full lines) with the corresponding values of Ref. 5 (dashed lines).

It should also be noted that the observations of Julienne et al. i.e., that the non L.T.E. properties oxygen plasmas practically do not depend on the forbidden collisional transitions and on the two low lying excited states, are true for recombining oxygen plasmas at low electron densities ($10^8 - 10^{12}$ cm^{-3}). This behaviour is also found in our plasmas, as can be appreciated from Fig. 7 for the α coefficients. As the electron density increases, the α values become however sensitive to the forbidden transitions and to the low lying excited states.

The situation is completely different for the coefficient S, which strongly depends on the forbidden transitions and on the two low lying excited states, as discussed before. These coefficients have not been calculated, however, by Julienne et al., because these authors were interested only into recombining plasmas.

Conclusions

In the present paper we have discussed several problems arising in the calculation of non L.T.E. properties of atomic oxygen plasmas.

In particular we have stressed the importance of the allowed and forbidden collisional transitions and of the two low lying excited states of oxygen atoms in affecting such properties. The satisfactory agreement observed between the present results and the corresponding experimental ones indicate that any theoretical determination of non L.T.E. properties should include as relevant species in the oxygen plasma the two low lying excited states as well as the states $3s'\,{}^1D^0$ and $3s'\,{}^3D^0$. Future improvement of the collisional cross sections should yield a better agreement between theory and experiments.

Acknowledgements

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[1] M. Capitelli, E. Ficocelli, and E. Molinari, Z. Naturforsch. **26 a**, 672 [1971] and references quoted in this paper.
[2] C. Park, J. Quant. Spectr. Radiative Transfer **8**, 1633 [1968].
[3] A. Catherinot and A. Sy, Z. Naturforsch. **30 a**, 1143 [1975].
[4] E. S. Oran, J. Davis, and P. S. Julienne, NRL Memorandum Rep. 2577 [1973].
[5] P. S. Julienne, J. Davis, and H. Hyman, NRL Memorandum Rep. 2740 [1974].
[6] M. Cacciatore and X. M. Capitelli, J. Quant. Spectr. Radiative Transfer **16**, 325 [1976].
[7] M. Cacciatore and M. Capitelli, Z. Naturforsch. **30 a**, 48 [1975].
[8] H. W. Drawin, Article in "Reaction under Plasma Conditions", M. Venugopalan, Ed., John Wiley, New York 1971.
[9] C. Moore, NBS Circular 467 [1949].
[10] M. Gryzinski, Phys. Rev. **138**, A 336 [1965].
[11] E. Bauer and C. D. Bartky, J. Chem. Phys. **43**, 2466 [1969].
[12] D. R. Bates, A. E. Kingston, and R. W. P. McWhirter, Proc. Roy Soc. London **A 267**, 297; **A 270**, 150 [1962].
[13] M. Cacciatore and M. Capitelli, Z. Naturforsch. **29 a**, 1507 [1974].
[14] H. W. Drawin, Report EUR-CEA-FC 383 [1967].
[15] M. J. Seaton, Proc. Phys. Soc. London **79**, 1105 [1962].
[16] M. Mitchner and C. H. Kruger, Partially Ionized Gases, John Wiley, New York 1973.
[17] L. A. Jones, J. Quant. Spectr. Radiative Transfer **12**, 1083 [1975].