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Electronically excited states and transport properties of thermal plasmas: The reactive thermal conductivity

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The role of excited states in affecting the transport of ionization energy in thermal plasmas in the temperature range $10000 \leqslant T \leqslant 25000$ K is discussed by taking into account the dependence of diffusion cross sections on principal quantum number. The results show a strong effect at high pressure, while compensation effects reduce the role of excited states at atmospheric pressure. Extension of the results to nonequilibrium situations is discussed by presenting calculations of effective multicomponent diffusion coefficients. In this case also the presence of excited states dramatically affects these coefficients.

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I. INTRODUCTION

Many years ago an attempt to describe the dependence of the reactive thermal conductivity of an atmospheric hydrogen plasma on the presence of electronically excited states was presented [1]. The results showed a sort of compensation between the reactive thermal conductivity obtained by using "*usual*" cross sections and "*abnormal*" ones. For "*usual*" cross sections we mean cross sections involving excited states equal to the corresponding ground state cross sections. The "*abnormal*" cross sections include the dependence of transport cross sections on the principal quantum number n. The results in both cases were calculated by using the Butler and Brokaw [2] equation describing the transport of chemical enthalpy of a system of μ independent chemical (ionization) reactions and ν chemical species.

The aim of this paper is to further clarify the problem extending the results to higher pressures taking into account recent and old results for the dependence of diffusion type collision integrals for the interactions $H(n)$-H^+ and $H(n)$-$H(m)$ on principal quantum number n. These interactions strongly affect the diffusion of ionization energy in the temperature gradient. To a first approximation the diffusion cross sections for these interactions are given by two times the corresponding resonant charge and excitation transfer cross sections, i.e., for the processes

$$H(n)+H^+ \rightarrow H^+ + H(n),$$

$$H(n)+H(m) \rightarrow H(m)+H(n).$$

Resonant charge transfer cross sections, calculated by different authors [3–7], are essentially in good agreement. They show a strong increase of the cross sections as a function of principal quantum number n, between n^3 and n^4. This means that the diffusion of ions in the temperature gradient can be strongly slowed by the collisions with excited states (despite their small concentration compared with the ground state atoms) thus decreasing the transport of ionization enthalpy.

The aim of this paper is to quantitatively evaluate the dependence of reactive thermal conductivity on the presence of excited states for thermal plasmas at different pressures and temperatures trying also to extend the present results to nonequilibrium conditions.

The paper is organized in four parts. The first deals with the equations describing the reactive thermal conductivity. Then a second part follows dedicated to the calculation of diffusion type collision integrals for the interactions $H(n)$-$H(m)$ and $H(n)$-H^+. The third part presents the results also extending the ideas to nonequilibrium situations. Summary and future perspectives are discussed in the Conclusion.

II. METHOD OF CALCULATION AND RESULTS

A. Reactive thermal conductivity

The reactive thermal conductivity which describes the transport of chemical enthalpy through temperature gradients represents one of the most important contributions to the total thermal conductivity of a reactive gas [8]. This term can be calculated by the general theory of the diffusion fluxes [9] assuming a very compact and simple form under the hypothesis of local chemical equilibrium along the temperature gradient. For a system of μ independent chemical (dissociation, ionization) reactions and ν chemical species we can write [2,9]

$$\lambda_r = -\frac{1}{RT^2}\begin{vmatrix} A_{11} & \dots & A_{1\mu} & \Delta H_1 \\ \vdots & & \vdots & \vdots \\ A_{\mu 1} & \dots & A_{\mu\mu} & \Delta H_\mu \\ \Delta H_1 & \dots & \Delta H_\mu & 0 \end{vmatrix} \Bigg/ \begin{vmatrix} A_{11} & \dots & A_{1\mu} \\ \vdots & & \vdots \\ A_{\mu 1} & \dots & A_{\mu\mu} \end{vmatrix}, \tag{1}$$

where

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$$A_{ij}=\sum_{k=1}^{\nu-1}\sum_{l=k+1}^{\nu}\frac{RT}{D_{kl}p}x_kx_l\left(\frac{a_{ik}}{x_k}-\frac{a_{il}}{x_l}\right)\left(\frac{a_{jk}}{x_k}-\frac{a_{jl}}{x_l}\right) \tag{2}$$

and ΔH_i is the variation of enthalpy associated with ith reaction, p is the total pressure, T is the temperature in kelvin, D_{ij} is the binary diffusion coefficient of the ij pair, x_i is the molar fraction of ith component in the mixture, and a_{ij} is the stoichiometric coefficient of jth species in the ith reaction.

This equation is generally simplified by neglecting the off diagonal terms in both numerator and denominator [10].

We assume as in Ref. [1] the dissociation process (not important in the considered temperature interval) and ionization reactions

$$\mathrm{H}(n)\rightarrow \mathrm{H}^{+}+e,$$

where H(n) is an hydrogen atom with principal quantum number n. The equilibrium composition entering in Eq. (1) is simply obtained by using Saha and Boltzmann laws. First we calculate the equilibrium composition by considering only four species (H_2, H, H^+, e) and two reactions (dissociation and ionization) which take into account the total atomic hydrogen without distinction among the electronic states. Then we use a Boltzmann distribution for calculating the distribution of the electronic states of atomic hydrogen

$$n_i=n_T\frac{g_i}{Z(T)}e^{-E_i/k_BT}, \tag{3}$$

where n_i is the number density of ith atomic excited state, g_i is the degeneration of ith atomic excited state, E_i is the energy of ith atomic excited state, n_T is the total number density of atomic hydrogen, and $Z(T)$ is the electronic partition function of atomic hydrogen. The binary diffusion coefficients D_{ij} entering in Eq. (1) are calculated by the resonant charge and excitation exchange cross sections for the interaction H(n)-H^+ and H(n)-H(m), and by Coulomb cross sections for H^+-e interaction.

B. Diffusion type collision integrals

Cross sections for the process

$$\mathrm{H}(ns)+\mathrm{H}(mp)\rightarrow \mathrm{H}(mp)+\mathrm{H}(ns)$$

were calculated by using the following equation [11] for $s-p$ (allowed) transitions:

$$\sigma=3.36\pi\mu^2e^2\frac{1}{\hbar v}, \tag{4}$$

where v is the relative velocity of colliding atoms, related to collision energy, and μ the dipole moment matrix element between s and p electronic states. Mean excitation transfer cross sections for other kinds of allowed interactions ($p-d$, $d-f$, $f-g$, $\dots$) were estimated using a scaling procedure (5), through G functions [9]

$$\frac{\sigma_{1s-2p}}{G_{1s-2p}}=\frac{\sigma_{nd-mf}}{G_{nd-mf}}, \tag{5}$$

$$G(n,\ell;m,\ell-1)=\frac{1}{a_0^2}\left[\int_0^\infty dr\,r^3R_{n,\ell}R_{m,\ell-1}\right]^2, \tag{6}$$

where R is the radial wave function for atomic hydrogen.

In order to obtain the excitation transfer cross section for the generic process

$$\mathrm{H}(n)+\mathrm{H}(m)\rightarrow \mathrm{H}(m)+\mathrm{H}(n),$$

we have weighted each kind of allowed interaction arising from the possible values assumed by the orbital quantum number ℓ, with the number of molecular electronic states that correlate with specified asymptotic atomic states [12]

$$\sigma_{n-m}=\frac{\sum_i \omega_i\sigma_i}{\sum_i \omega_i}. \tag{7}$$

Cross sections involving principal quantum numbers up to $n=11$ and $m=12$ were calculated in the [1.0–10.0 eV] energy range.

A comparison of these results with those calculated by Nakamura *et al.* [13] and by Capitelli *et al.* [14] for the processes

$$\mathrm{H}(1s)+\mathrm{H}(2s,2p)\rightarrow \mathrm{H}(2s,2p)+\mathrm{H}(1s),$$

$$\mathrm{H}(1s)+\mathrm{H}(3s,3p,3d)\rightarrow \mathrm{H}(3s,3p,3d)+\mathrm{H}(1s)$$

shows a satisfactory agreement. The last results were calculated by the PSS (*perturbed stationary state*) method and the Firsov approximation by using Heitler-London potentials for all molecular states correlating with the given asymptotes.

As suggested by Dalgarno [15], fitting the cross section [Å^2] dependence on the relative speed v [cm/s] with relation

$$\sigma_{n-m}=\frac{1}{2}[\mathcal{A}-\mathcal{B}\ln(v)]^2, \tag{8}$$

we can derive analytic expression of diffusion type collision integral $\Omega^{(1,1)}$ [Å^2], in terms of the constants $\mathcal{A}$ and $\mathcal{B}$ [16].

$$\begin{aligned}\Omega^{(1,1)}=\frac{1}{\pi}\Bigg[&\mathcal{A}^2-\mathcal{A}\mathcal{B}\ln(4R)+\left(\frac{\mathcal{B}\ln(4R)}{2}\right)^2\\&+\frac{\mathcal{B}\zeta}{2}(\mathcal{B}\ln(4R)-2\mathcal{A})+\frac{\mathcal{B}^2}{4}\left(\frac{\pi^2}{6}-\sum_{n=1}^{2}\frac{1}{n^2}+\zeta^2\right)\\&+\frac{\mathcal{B}}{2}(\mathcal{B}[\ln(4R)+\zeta]-2\mathcal{A})\ln\left(\frac{T}{M}\right)\\&+\left(\frac{\mathcal{B}}{2}\ln\left(\frac{T}{M}\right)\right)^2\Bigg],\end{aligned} \tag{9}$$

where R is the gas constant, $\zeta=\Sigma_{n=1}^{2}(1/n)-\overline{\gamma}$, with $\overline{\gamma}$ Euler's constant and M is the molecular weight. The temperature

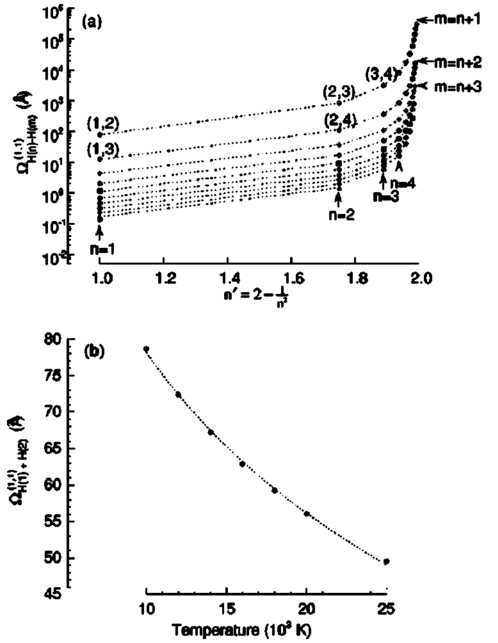

FIG. 1. (a) Diffusion-type collision integrals as a function of $n' = (2 - 1/n^2)$, for different H(n)-H(m) interactions, at $T = 10^4$ K; (b) temperature dependence of collision integrals for interaction H(1)-H(2).

dependence of $\Omega^{(1,1)}$ in the range $[10^4\text{–}2.5\times10^4\ \text{K}]$ is reproduced using a logarithmic relation

$$\Omega^{(1,1)}(T) = a_1 + a_2 \ln(T). \tag{10}$$

A sample of results is reported in Figs. 1(a) and 1(b) while the a_1, a_2 values, for selected processes, are reported in Table I. Note the dramatic increase of collision integrals diffusion type for the interaction H(n)-H($m=n+1$) with increasing n as well as the strong decrease of collision integrals for multiquantum transitions ($n \rightarrow m = n+2, n+3, \ldots$). The temperature dependence of the collision integrals is on the contrary very weak [Fig. 1(b)].

TABLE I. Fitting coefficients, a_i, for diffusion type collision integrals, $\Omega^{(1,1)}$ [Eq. (10)] for single quantum transitions.

Interaction	a_1	a_2
H(1)-H(2)	3.709×10^{2}	-3.178×10^{1}
H(2)-H(3)	3.913×10^{3}	-3.353×10^{2}
H(3)-H(4)	1.460×10^{4}	-1.251×10^{3}
H(4)-H(5)	3.829×10^{4}	-3.281×10^{3}
H(5)-H(6)	8.256×10^{4}	-7.074×10^{3}
H(6)-H(7)	1.568×10^{5}	-1.344×10^{4}
H(7)-H(8)	2.720×10^{5}	-2.330×10^{4}
H(8)-H(9)	4.411×10^{5}	-3.780×10^{4}
H(9)-H(10)	6.785×10^{5}	-5.814×10^{4}
H(10)-H(11)	1.000×10^{6}	-8.573×10^{4}
H(11)-H(12)	1.425×10^{6}	-1.221×10^{5}

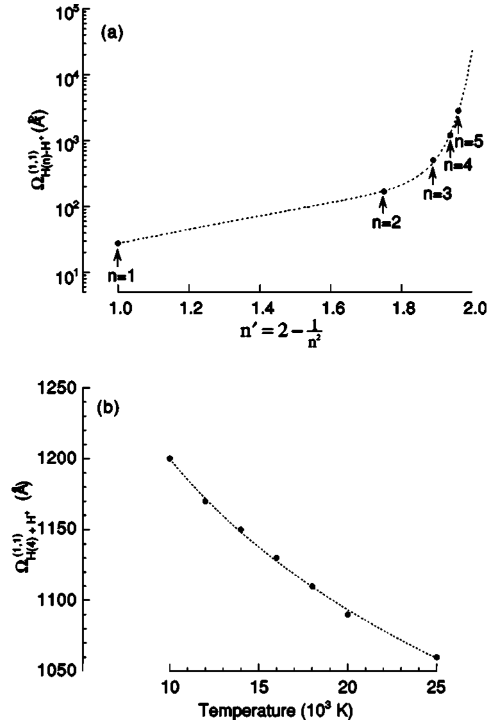

FIG. 2. (a) Diffusion-type collision integrals as a function of $n' = (2 - 1/n^2)$, for H(n)-H$^+$ interactions, at $T = 10^4$ K; (b) temperature dependence of collision integrals for interaction H(4)-H$^+$.

Diffusion type collision integrals $\Omega^{(1,1)}$ for the process

$$H(n) + H^+ \rightarrow H^+ + H(n)$$

calculated by Capitelli *et al.* [17], were fitted as a function of a modified energy scale, $n' = (2 - 1/n^2)$, using the following analytical expression [18]

$$\Omega^{(1,1)} = \exp(c(T)n'^{0.77} + \exp(15.9n' - 30.3)), \tag{11}$$

with $c(T) = 3.519T^{-0.027321}$.

Expression (11) can be used to calculate the Ω values for $n > 5$ at different temperatures in the range $[10^4\text{–}2.5\times10^4\ \text{K}]$. The present results are based on the calculation of resonant charge transfer cross sections performed many years ago by Capitelli and Ficocelli [6] which in any case are in satisfactory agreement with corresponding calculations by other authors [3–5,7]. Resonant charge transfer dramatically increase with n having a dependence between n^3 and n^4.

A sample of diffusion type collision integrals are reported in Figs. 2(a) and 2(b). They show a dramatic increase with the principal quantum number n, having a weak dependence on temperature.

C. Results and discussion

Let us now examine the reactive thermal conductivity of an hydrogen plasma calculated by including the ionization reactions involving the first 12 electronic states in the ionization scheme as well as the dissociation reaction [i.e., we consider $\mu = 13$ independent chemical (1 dissociation, 12 ionizations) reactions and $\nu = 15$ independent chemical species]. These results will be compared with the corresponding ones obtained by imposing to all excited states the same

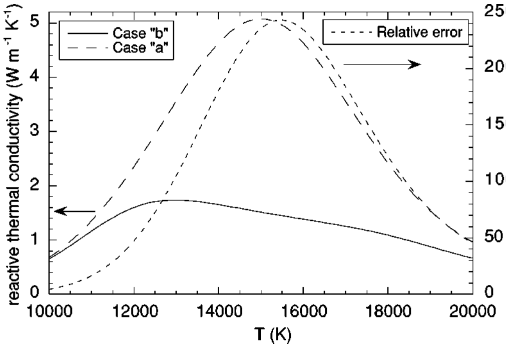

FIG. 3. Reactive thermal conductivity, by using "*usual*" (a) and "*abnormal*" (b) collision integrals at $p=1$ atm, calculated by considering only diagonal terms in Eq. (1).

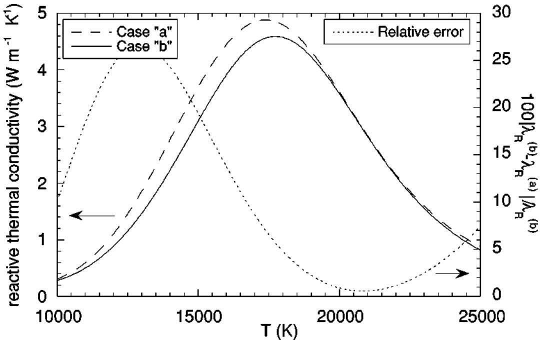

FIG. 5. Reactive thermal conductivity and relative error calculated by using "*usual*" (a) and "*abnormal*" (b) collision integrals at $p=10$ atm.

collision integrals as the ground state. The last is the usual procedure adopted in the literature.

We start our analysis by considering in Eq. (1) only the diagonal terms, an approximation which is known to work very well for reactive neutral gases. Figure 3 compares the reactive thermal conductivity for an atmospheric hydrogen plasma calculated with the two sets of cross sections (usual and abnormal). We can see that in this case the presence of excited states with their own cross sections is such to strongly decrease the reactive thermal conductivity (see also the relative error curve).

This behavior disappears at $p=1$ atm when we calculate Eq. (1) inserting also the off diagonal terms. In this case (see Fig. 4) a sort of compensation between diagonal and off diagonal terms arises having as a consequence the practical coincidence of the two cases. This point confirms the results of Ref. [1].

This kind of compensation disappears with increasing pressure (see Figs. 5, and 6). For the higher pressure examined in the present study (Fig. 6), using the complete Eq. (1) and the same number of electronically excited states (again up to $n=12$), a difference up to factor 2 in the results can be appreciated. This point indicates that the role of electronically excited states in affecting the reactive thermal conductivity in LTE plasmas cannot be neglected. We should however point out that the use of the same number of excited states for different pressures can be open to question. One should expect infact that the number of excited states to be considered in the relevant equations decreases with increasing pressure. To study this point we have calculated the reactive thermal conductivity by adding step by step the ionization reactions in Eq. (1). We start by considering one ionization reaction involving only the ground state, i.e.,

$$\mathrm{H}(1)\rightarrow\mathrm{H}^{+}+e.$$

We proceed by inserting two ionization reactions and two excited states, i.e.,

$$\mathrm{H}(1)\rightarrow\mathrm{H}^{+}+e,$$

$$\mathrm{H}(2)\rightarrow\mathrm{H}^{+}+e.$$

The procedure is repeated up to $n=12$.

Corresponding results have been reported in Figs. 7(a) and 7(b) and 8(a) and 8(b) for $p=1$ atm and in Figs. 9(a) and 9(b) and 10(a) and 10(b) for $p=100$ atm. In all figures the case (a) refers to "*usual*" cross sections while case (b) refers to "*abnormal*" ones. At $p=1$ atm the results for case (a) and (b) look very similar when we consider the same number of ionization reactions and excited states [Figs. 7(a) and 7(b)], while strong differences can be appreciated when the number of excited states is considered constant (12 levels) in all the considered cases [Figs. 8(a) and 8(b)]. Let us consider the one ionization case in Figs. 8(a) and 8(b). In this

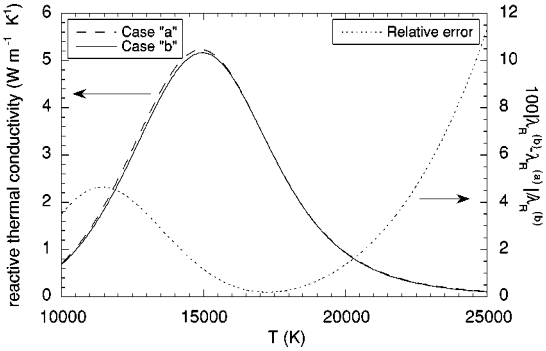

FIG. 4. Reactive thermal conductivity and relative error calculated by using "*usual*" (a) and "*abnormal*" (b) collision integrals at $p=1$ atm.

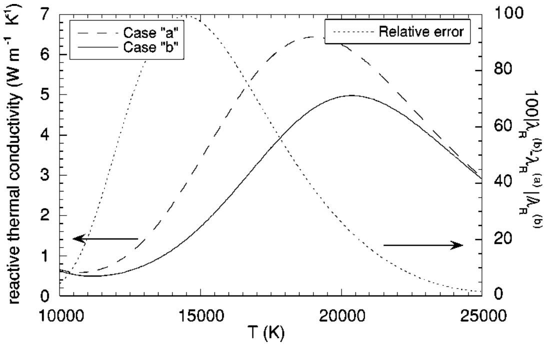

FIG. 6. Reactive thermal conductivity and relative error calculated by using "*usual*" (a) and "*abnormal*" (b) collision integrals at $p=100$ atm.

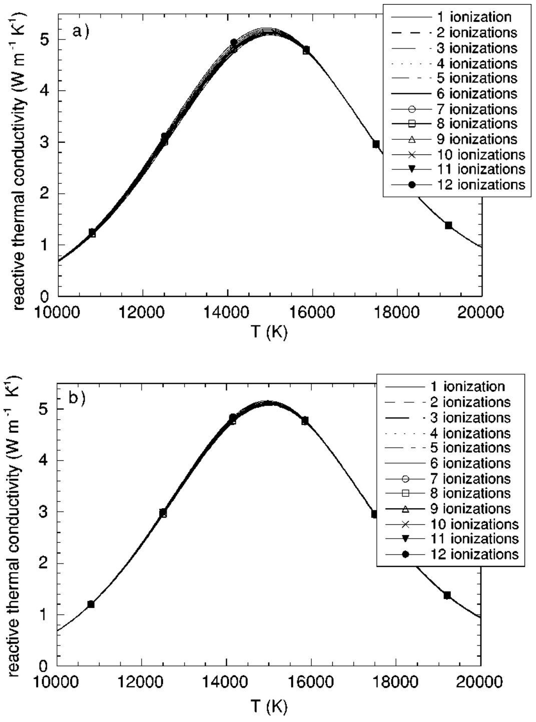

FIG. 7. Reactive thermal conductivity as a function of temperature calculated by using "*usual*" (a) and "*abnormal*" (b) collision integrals at $p=1$ atm, by considering as many ionization reactions as excited energy levels.

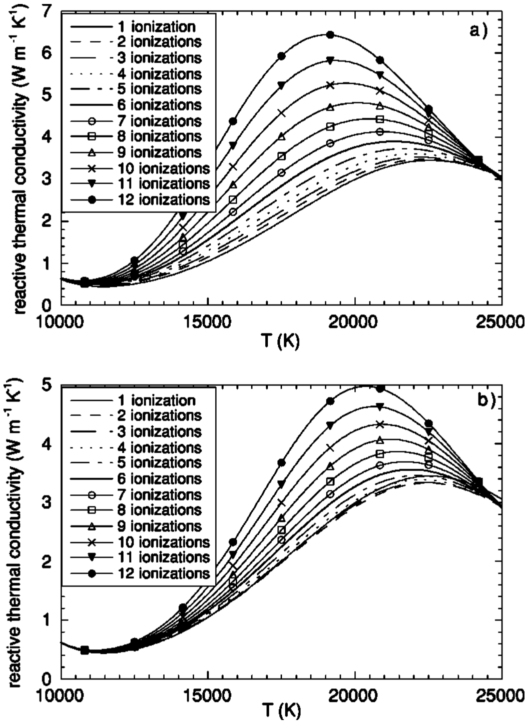

FIG. 9. Reactive thermal conductivity as a function of temperature calculated by using "*usual*" (a) and "*abnormal*" (b) collision integrals at $p=100$ atm, by considering as many ionization reactions as excited energy levels.

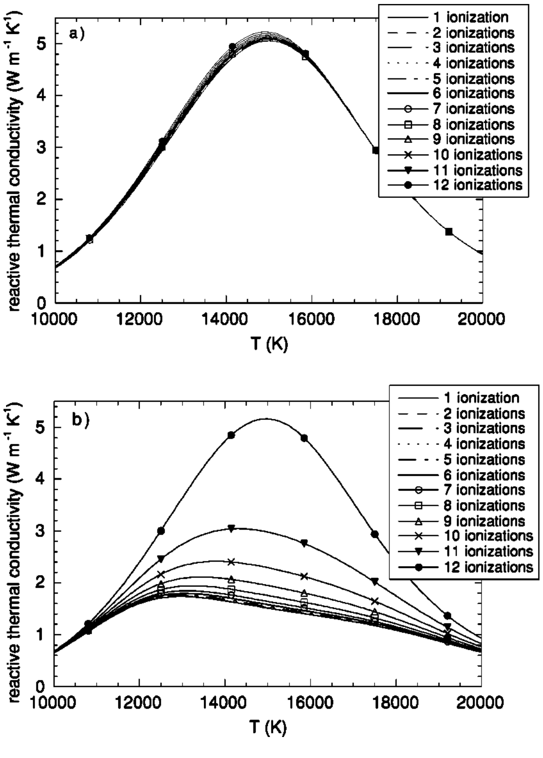

FIG. 8. Reactive thermal conductivity as a function of temperature calculated by using "*usual*" (a) and "*abnormal*" (b) collision integrals at $p=1$ atm, by considering a different number of ionization reactions and the same number (12) of excited electronic levels.

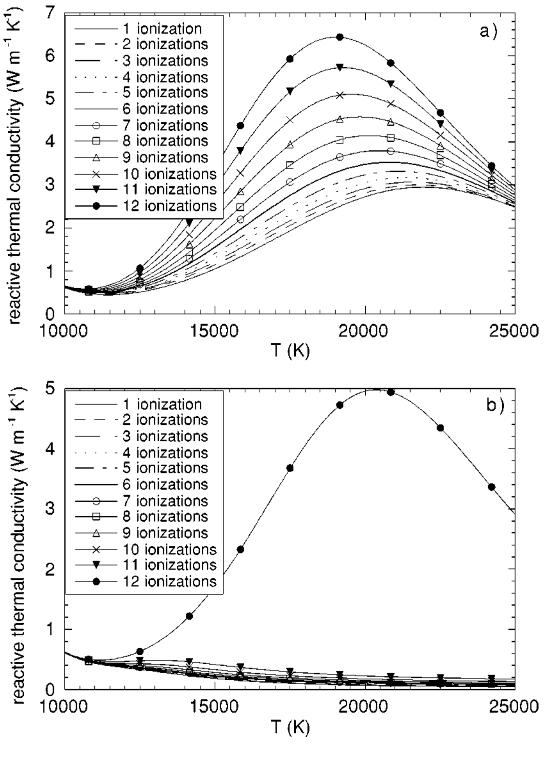

FIG. 10. Reactive thermal conductivity as a function of temperature calculated by using "*usual*" (a) and "*abnormal*" (b) collision integrals at $p=100$ atm, by considering a different number of ionization reactions and the same number of excited electronic levels.

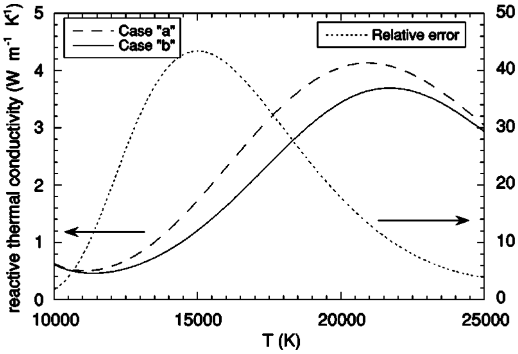

FIG. 11. Reactive thermal conductivity calculated by using "*usual*" (a) and "*abnormal*" (b) collision integrals at $p=100$ atm, with seven ionization reactions.

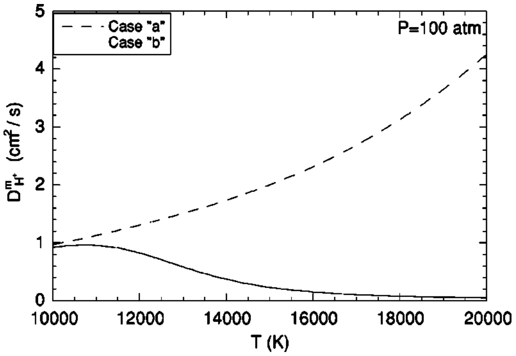

FIG. 13. Effective diffusion coefficient for H^+ in the mixture as a function of temperature at $p=100$ atm calculated according to Eq. (13).

case we consider the first ionization reaction in the presence of the concentration of 12 excited states 11 of which are considered as inert species. In this case strong differences are observed when using usual or abnormal cross sections.

The situation becomes more complicated at $p=100$ atm when the compensation effects between diagonal and off-diagonal terms of Eq. (1) becomes weak. We can appreciate [Figs. 9(a) and 9(b)] a progressive increase of the reactive thermal conductivity with the increase of the number of ionization reactions either when we use usual cross sections or abnormal ones. In this case we are considering as many ionization reactions as many excited states. The situation becomes dramatic, at $p=100$ atm, when part of the excited states is considered as inert species [see Figs. 10(a) and 10(b)].

Coming back to the results of Figs. 7(a) and 7(b) and 9(a) and 9(b) we can reinterpret them as a result of a cutoff criterion to cut the electronic partition function of atomic hydrogen. Keeping in mind the multiciplity of cutoff criteria [19] we select a very simple and intuitive criterion that one which includes in the electronic partition function all the electronic states with radius less than the average distance between particles. By considering the Bohr radius of electronic states we get the following equation

$$a_0 n_{max}^2 = \left(\frac{1}{n'}\right)^{1/3}, \tag{12}$$

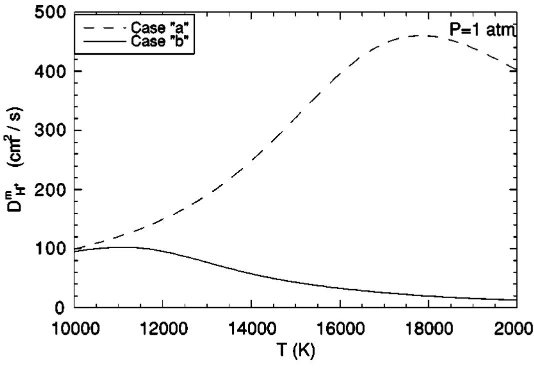

FIG. 12. Effective diffusion coefficient for H^+ in the mixture as a function of temperature at $p=1$ atm calculated according to Eq. (13).

where a_0 is the Bohr radius of the ground state and $n' = p/kT$ is the total number density. Application of this equation to $p=100$ atm and $10000 \leqslant T \leqslant 25000$ K gives an approximate value of $n_{max}=7$. In Fig. 11 we have reported the results obtained by inserting in Eq. (1) seven ionization reactions and seven excited states. The differences between the results obtained with the two sets of cross sections are reduced compared with the 12 ionizations case reaching however a maximum of 40% (see Fig. 11). The present results refer to a quasiequilibrium conditions.

Under nonequilibrium conditions the transport of ionization energy should be proportional to a first approximation to an effective multicomponent diffusion coefficient D_i^m given by the following equation [20]

$$D_i^m = \frac{M_i(1-\xi_i)}{\bar{M}\sum_{j=1,j\neq i}^{\nu} \frac{x_j}{D_{ij}}}, \tag{13}$$

where $\bar{M}$ is the mixture molar mass, ξ_i is the mass fraction of ith component, and M_i is the molar mass of the ith component.

The effective multicomponent diffusion coefficients for H^+ diffusing in the plasma composed by excited atoms including the ground state and electrons calculated by using

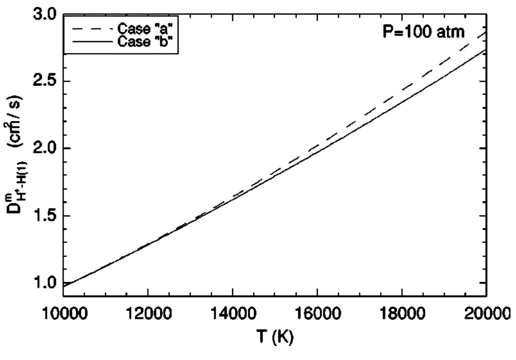

FIG. 14. Multicomponent diffusion coefficient of the pair H^+-H(1) as a function of temperature at $p=100$ atm calculated according to Eq. (14).

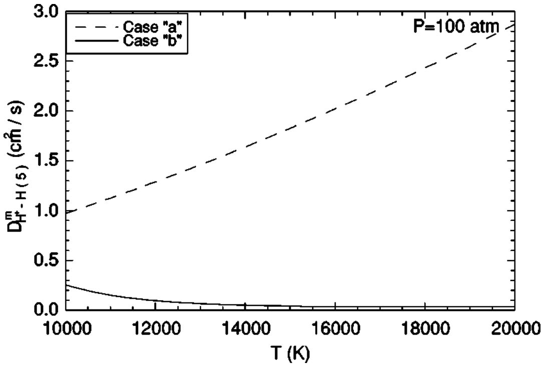

FIG. 15. Multicomponent diffusion coefficient of the pair H^+-H(5) as a function of temperature at $p=100$ atm calculated according to Eq. (14).

Eq. (13) have been reported as a function of temperature in Figs. 12, and 13 for different pressures and for different hypotheses on the diffusion cross sections. Again we observe a dramatic decrease of the effective multicomponent diffusion coefficient when the excited states are considered with their own cross sections [case (b) in the two figures]. Roughly speaking the effective multicomponent diffusion coefficient calculated according to Eq. (13) resembles to some extent to the calculation of reactive thermal conductivity when the off diagonal terms are disregarded in Eq. (1).

On the other hand, we can calculate the multicomponent diffusion coefficients of the couple ij in the presence of all other species. To this end we use the following equation [9]

$$D^m_{ij}=\frac{1}{M_j}\left(\sum_k x_k M_k\right)\frac{K^{ji}-K^{ii}}{|K|}, \tag{14}$$

where $K_{ii}=0$ and

$$K_{ij}=\frac{x_i}{D_{ij}}+\frac{M_j}{M_i}\sum_{k\neq i}\frac{x_k}{D_{ik}}, \quad i\neq j. \tag{15}$$

$|K|$ is the determinant of K_{ij} and K^{ji} are the minors:

$$K^{ji}=(-1)^{i+j}\begin{vmatrix} 0 & \dots & K_{1,i-1} & K_{1,i+1} & \dots & K_{1,\nu} \\ \vdots & & \vdots & \vdots & & \vdots \\ K_{j-1,1} & \dots & K_{j-1,i-1} & K_{j-1,i+1} & \dots & K_{j-1,\nu} \\ K_{j+1,1} & \dots & K_{j+1,i-1} & K_{j+1,i+1} & \dots & K_{j+1,\nu} \\ \vdots & & \vdots & \vdots & & \vdots \\ K_{\nu,1} & \dots & K_{\nu,i-1} & K_{\nu,i+1} & \dots & 0 \end{vmatrix}. \tag{16}$$

These diffusion coefficients are not symmetric as binary diffusion coefficients and are more specific than binary diffusion coefficients because they take into account the specific nature of the relevant mixture.

Figures 14 and 15 report these coefficients as a function of temperature for the couples H^+-H(1) and H^+-H(5) at $p=100$ atm calculated according to the two sets of cross sections. We note that the presence of excited states with their cross sections plays a role for the H^+-H(5) multicomponent diffusion coefficient having a small role for the H^+-H(1) multicomponent diffusion coefficient. This means that the presence of nondiagonal terms in the multicomponent diffusion coefficients is such to reduce the influence of excited states on the H^+-H(1) multicomponent diffusion coefficient.

III. CONCLUSIONS

In the present paper we have shown the role of excited states in affecting the reactive thermal conductivity of an LTE (local thermodynamic equilibrium) plasma. The present calculations while confirming the compensation effect for atmospheric pressure plasmas [1] show however a strong dependence of reactive thermal conductivity on the presence of excited states at higher pressures. Moreover the effective multicomponent diffusion coefficients which can be used for nonequilibrium situations show a dramatic dependence on the presence of excited states. This point should push further work for the evaluation of the dependence of the enthalpy flow under either for nonequilibrium situations [20] or for multitemperature plasmas [21].

As a conclusion we can say that the presence of excited states with their abnormal cross sections can open important perspectives in the transport theory of partially ionized gases. Study is now in progress to evaluate the role of excited states in affecting the translational thermal conductivity and viscosity of thermal and nonthermal plasmas. Also in this case the results reported in Ref. [17] should be rediscussed in light of the recent progress in the cross sections involving H(n)-H(n) and e-H(n) interactions [22–24].

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