

Transport Properties of Electronically Excited N_2/N and O_2/O Mixtures

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Abstract. Chemically non-equilibrium neutral gas mixture flows of N_2/N and O_2/O with electronic excitation are studied. The one-temperature model of transport properties taking into account electronic states of both molecules and atoms is developed. The generalized Chapman–Enskog method is applied to derive the closed set of governing equations and to evaluate the transport terms. The transport coefficients of thermal conductivity, diffusion and thermal diffusion, shear and bulk viscosity, as well as the Prandtl number are calculated in the temperature range 500–50000 K for various mixture compositions. Contribution of the electronic degrees of freedom to the transport properties is found to be important, especially for atomic species.

Keywords: Kinetic theory of transport process, Transport coefficients, Electronic excitation

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INTRODUCTION

In non-equilibrium fluid dynamics, great attention is focused on the study of transport processes, that is important for various applications in aerospace and plasma sciences. During the reentry of an aircraft into a planetary atmosphere, the temperature grows sharply behind a shock wave up to thousands degrees Kelvin, which results in the excitation of internal degrees of freedom, dissociation and ionization processes. Under such conditions, the account for electronic excitation becomes necessary for the modeling of high-temperature gas mixture flows. While the role of rotational and vibrational degrees of freedom in the energy transfer is widely studied in the literature (see Ref. [1] and references therein), the influence of electronic excitation of molecules and, especially, atoms on the transport phenomena is not understood until the present time. In recent papers [2, 3], the near-equilibrium plasma of atomic hydrogen with electronically excited states was studied, and the contribution of electronic levels to thermal conductivity was found to be important. A theoretical model of transport properties in a non-equilibrium mixture flow taking into account electronic excitation of both molecules and atoms was proposed recently in Ref. [4].

The purpose of the present paper is to generalize the model proposed in [4] for non-equilibrium flows of N_2/N and O_2/O mixtures and calculate heat conductivity, shear and bulk viscosity, diffusion and thermodiffusion coefficients in the temperature range 500–50000 K. The influence of electronic excitation on all transport coefficients is evaluated. On the basis of the calculated transport coefficients and specific heats, the Prandtl number is estimated. Ionization processes are not considered in the present paper since its objective is to study the pure effect of electronic excitation. In future work we plan to include ionization processes.

MACROSCOPIC PARAMETERS AND GOVERNING EQUATIONS

We consider a one-temperature chemically non-equilibrium flow of a gas mixture for which the following relation between characteristic times holds:

$$\tau_{tr} < \tau_{rot} < \tau_{vibr} < \tau_{el} \ll \tau_{react} \sim \theta. \quad (1)$$

Here τ_{tr} , τ_{rot} , τ_{vibr} , τ_{el} , and τ_{react} are the characteristic times for translational, rotational, vibrational and electronic relaxation, and chemical reactions; θ is the mean time of the variation of gas-dynamic parameters. For this relation, chemical reactions can be considered on the basis of the maintaining Maxwell–Boltzmann distributions over the velocity and internal energy levels.

In the present study, we take into account rotational, vibrational and electronic modes of molecules as well as electronically excited states of atomic species. Thus the internal energy of molecules and atoms is modeled as follows [4]:

$$\varepsilon_l^c = \begin{cases} \varepsilon_{nij}^{mol} = \varepsilon_{el}(n) + \varepsilon_{vibr}(n, i) + \varepsilon_{rot}(n, i, j), \\ \varepsilon_n^{at} = \varepsilon_{el}(n), \end{cases} \quad (2)$$

where ε_{el} , ε_{vibr} , and ε_{rot} are the energies of the electronic, vibrational and rotational degrees of freedom respectively (n, i, j are the correspondingly quantum numbers, c is the chemical species). Hereafter we denote by l the set of quantum numbers n, i, j , for molecules and the electronic level n for atoms. For the calculation of the internal energy of molecules we use the spectroscopic data from [5], the electronic states of atoms are provided in Ref. [6]. The electronic energy is taken from the tables of the spectroscopic data, the vibrational energy for each electronic state is calculated on the basis of the Morse potential for anharmonic oscillators, the rotational energy is simulated taking into account its dependence on the electronic and vibrational level [6].

The closed set of governing equations for the macroscopic parameters taking into account electronic degrees of freedom of both molecules and atoms is derived from the kinetic equations for distribution function $f_{cl}(\mathbf{r}, \mathbf{u}, t)$ using the generalized Chapman–Enskog method [1, 4]. In the absence of external forces, the governing equations have the following form:

$$\frac{dn_c}{dt} + n_c \nabla \cdot \mathbf{v} + \nabla \cdot (n_c \mathbf{V}_c) = R_c^{react}, \quad c = 1, \dots, L, \quad (3)$$

$$\rho \frac{d\mathbf{v}}{dt} + \nabla \cdot \mathbf{P} = 0, \quad (4)$$

$$\rho \frac{dU}{dt} + \nabla \cdot \mathbf{q} + \mathbf{P} : \nabla \mathbf{v} = 0, \quad (5)$$

here n_c is the number density of species c , \mathbf{v} is the gas velocity, L is the number of chemical species, U is the total specific energy including electronic degrees of freedom, \mathbf{V}_c is the diffusion velocity, R_c^{react} is the production term due to chemical reactions, ρ is the mixture density, \mathbf{P} is the pressure tensor, \mathbf{q} is the heat flux.

ZERO AND FIRST-ORDER APPROACHES

In the zero-order approximation of the modified Chapman–Enskog method, the distribution functions are obtained in the form:

$$f_{cl}^{(0)} = \left(\frac{m_c}{2\pi kT} \right)^{3/2} \frac{n_c s_{cl}}{Z_c^{int}(T)} \exp\left(-\frac{m_c \mathbf{c}_c^2}{2kT} - \frac{\varepsilon_l^c}{kT} \right), \quad (6)$$

where m_c is the mass of a particle of c species, T is the temperature, $\mathbf{c}_c = \mathbf{u}_c - \mathbf{v}$ is the peculiar velocity, k is the Boltzmann constant, s_{cl} is the statistical weight for the internal state l , $Z_c^{int}(T)$ is the equilibrium internal partition function:

$$Z_c^{int}(T) = \sum_l s_{cl} \exp\left(-\frac{\varepsilon_l^c}{kT} \right).$$

The distribution functions (6) represent the local equilibrium Maxwell–Boltzmann distributions of molecules and atoms over the velocity and internal energy, and non-equilibrium distribution over chemical species. A substantial difference from the models developed earlier is that for atoms, we obtain not only the Maxwell velocity distribution, but also the Boltzmann distribution over the electronic energy levels.

The Chapman–Enskog method makes it possible to express, in each approximation, the transport terms as functions of the main macroscopic parameters and their spatial derivatives. In the zero-order approximation, the pressure tensor takes a diagonal form $\mathbf{P} = p\mathbf{I}$ (p is the hydrostatic pressure, \mathbf{I} is the unit tensor), whereas the remaining transport terms are equal to zero: $\mathbf{V}_c = \mathbf{q} = 0$.

In the first-order approximation of the modified Chapman–Enskog method, the distribution function is obtained in the following form

$$f_{cl}^{(1)} = f_{cl}^{(0)} \left(-\frac{1}{n} \mathbf{A}_{cl} \cdot \nabla \ln T - \frac{1}{n} \sum_d \mathbf{D}_{cl}^d \cdot \mathbf{d}_d - \frac{1}{n} \mathbf{B}_{cl} : \nabla \mathbf{v} - \frac{1}{n} F_{cl} \nabla \cdot \mathbf{v} - \frac{1}{n} G_{cl} \right) \quad (7)$$

The first-order correction depends on the gradients all macroscopic parameters and contains the unknown functions \mathbf{A}_{cl} , \mathbf{D}_{cl} , \mathbf{B}_{cl} , F_{cl} , and G_{cl} which are found from the linear integral equations similar to those derived in [1].

Using the procedure of the modified Chapman–Enskog method, we derive the expressions for the pressure tensor, diffusion velocity and energy flux in a viscous conductive flow:

$$\mathbf{P} = (p - p_{rel})\mathbf{I} - 2\eta\mathbf{S} - \zeta\nabla \cdot \mathbf{v}\mathbf{I}, \quad (8)$$

$$\mathbf{V}_c = -\sum_d D_{cd}\mathbf{d}_c - D_{Tc}\nabla \ln T, \quad (9)$$

$$\mathbf{q} = -\lambda'\nabla T - p\sum_c D_{Tc}\mathbf{d}_c + \sum_c \rho_c h_c \mathbf{V}_c. \quad (10)$$

Here \mathbf{S} is the deformation rate tensor, \mathbf{d}_c is the diffusive driving force, h_c is the specific enthalpy of species c .

In the equations (8)–(10), η , ζ are the shear and bulk viscosity coefficients, p_{rel} is the relaxation pressure, D_{cd} , D_{Tc} are the diffusion and thermal diffusion coefficients, $\lambda' = \lambda_{tr} + \lambda_{int}$ is the partial thermal conductivity coefficient including contributions of the translational and internal degrees of freedom. Note, that the normal mean stress in this case includes the terms $\zeta\nabla \cdot \mathbf{v}$ and p_{rel} associated respectively to the flow compressibility and to the contribution of non-equilibrium chemical reactions.

TRANSPORT COEFFICIENTS

In order to calculate the transport coefficients the unknown functions \mathbf{A}_{cl} , \mathbf{D}_{cl} , \mathbf{B}_{cl} , F_{cl} , and G_{cl} are expanded into the series of the Sonine polynomials in the reduced peculiar velocity and Waldmann–Trübenbacher polynomials in the internal energy [1]. The transport coefficients are expressed in terms of the expansion coefficients:

$$\lambda' = \sum_c \frac{5}{4} k \frac{n_c}{n} a_{c,10} + \sum_c \frac{m_c}{2} \frac{n_c}{n} c_{int,c} a_{c,01}, \quad (11)$$

$$D_{cd} = \frac{1}{2n} d_{c,0}^d, \quad (12)$$

$$D_{Tc} = -\frac{1}{2n} a_{c,00}, \quad (13)$$

$$\eta = \frac{kT}{2} \sum_c \frac{n_c}{n} b_{c,0}, \quad (14)$$

$$\zeta = -kT \sum_c \frac{n_c}{n} f_{c,10}, \quad (15)$$

$$p_{rel} = kT \sum_c \frac{n_c}{n} g_{c,10}. \quad (16)$$

$c_{int,c}$ is the internal specific heat at constant volume. We use the standard procedure of the Chapman–Enskog method [1], and show that the integral equations for the unknown functions are reduced to the transport linear systems of algebraic equations involving the bracket integrals as coefficients. The bracket integrals are simplified applying the commonly used assumptions proposed by Mason and Monchick [7]. The transport coefficients are then calculated numerically as the solutions of the transport linear systems using the Gauss method or iterative technique [8].

Finally, all transport coefficients are expressed in terms of the standard collision $\Omega_{cd}^{(l,r)}$ integrals and integrals β depending on the energy variation ΔE in inelastic collisions. $\Omega_{cd}^{(l,r)}$ integrals are calculated using the data from [9]. Integrals β for rotational and vibrational energy exchanges are usually connected to the relaxation times of corresponding internal modes. For the electronic transitions, there is no accurate data on the relaxation times. We propose to approximate the corresponding integral using the deactivation rate constants for the transition from the first to the ground electronic state. The deactivation rate constants are taken from [10, 11]: $k_{10N} = 10^{-19} \text{ m}^3/\text{c}$; $k_{10O} = 8 \cdot 10^{-18} \text{ m}^3/\text{c}$.

TABLE 1. Contribution of the translational and internal modes to the total thermal conductivity coefficient λ' of species, %

T, K	N		N ₂			O		O ₂		
	$\lambda_{tr,N}$	$\lambda_{int,N}$	λ_{tr,N_2}	λ_{rv,N_2}	λ_{int,N_2}	$\lambda_{tr,O}$	$\lambda_{int,O}$	λ_{tr,O_2}	λ_{rv,O_2}	λ_{int,O_2}
500	100	0	72.8	27.2	27.2	98.0	2.0	69.4	30.6	30.6
1000	100	0	66.1	33.9	33.9	99.4	0.6	62.1	37.9	37.9
5000	89.8	10.2	56.3	43.6	43.7	95.6	4.4	50.8	41.7	49.2
10000	70.1	29.9	47.9	40.5	52.1	89.7	10.3	49.0	41.5	51.0
15000	46.7	53.3	32.4	28.6	67.6	66.0	34.0	58.5	38.8	41.5
20000	21.4	78.6	33.0	27.8	67.0	30.0	70.0	69.2	32.9	30.8
25000	23.5	76.5	42.4	31.7	57.6	23.2	76.8	77.3	26.4	22.7
30000	38.3	61.7	53.9	34.2	46.1	30.1	69.9	83.0	20.9	17.0
35000	57.0	43.0	63.9	33.9	36.1	43.6	56.4	86.9	16.7	13.1
40000	72.2	27.8	71.8	31.7	28.2	58.3	41.7	89.6	13.4	10.4
45000	82.2	17.8	77.6	28.7	22.4	70.6	29.3	91.6	11.0	8.4
50000	88.3	11.7	82.0	25.6	18.0	79.5	20.5	93.1	9.1	6.9

RESULTS AND DISCUSSION

The transport coefficients were calculated for the N_2/N and O_2/O mixtures in the temperature range 500–50000 K using the approach developed above. The results show that electronic excitation has a negligible effect on the coefficients of shear viscosity, diffusion and thermal diffusion is negligible, whereas the effect on the thermal conductivity coefficients is significant.

The coefficients of thermal conductivity $\lambda_{tr,c}$ (taking into account only the translation energy), $\lambda_{int,c}$ (accounting for the total internal energy), and $\lambda_{rv,c}$ (only rotational-vibrational energy of the ground electronic state is taken into account) of the components of N_2/N and O_2/O mixtures are given in Table 1 as functions of T . The excitation of electronic degrees of freedom influences substantially the thermal conductivity. Thus, neglecting the electronic states results in the significant underestimation of the molecular internal thermal conductivity: for the temperature range 15000–20000 K, the coefficient λ_{int,N_2} is more than twice larger than the coefficient λ_{rv,N_2} calculated neglecting the electronic states. The contribution of the electronic states to the thermal conductivity of atomic species in the temperature range 12000–30000 K is even higher: for $T \approx 20000$ K, the coefficient of internal thermal conductivity for atoms $\lambda_{int,N}$ is approximately 4 times larger than the corresponding translational thermal conductivity coefficient $\lambda_{tr,N}$. The same situation holds for O and O₂: the coefficient λ_{int,O_2} is larger than the coefficient λ_{rv,O_2} in the temperature range 5000–20000 K. For atomic oxygen, the contribution of electronic states to λ' prevails in the temperature range 20000–35000 K. For example, the coefficient of internal thermal conductivity $\lambda_{int,O}$ is 3 times larger than the translational thermal conductivity coefficient $\lambda_{tr,O}$ for $T \approx 25000$ K. It is interesting to note that in the temperature range 40000–50000 K for N₂ and 20000–50000 K for O₂ λ_{rv} is slightly larger than λ_{int} . This effect is connected with the similar behavior of the specific heats at constant pressure c_p , which is discussed in [4].

In Fig. 1a, the total thermal conductivity λ' as a function of T is presented for three cases: $x_{mol} = 1; x_a = 1; x_{mol} = x_a = 0.5$ (x_{mol} , x_a are the molar fractions of molecules and atoms). For atoms, the thermal conductivity coefficient has a strong maximum in the temperature range $T = 20000 - 25000$ K. The thermal conductivity coefficient λ' of molecules also increases with the temperature. However, it remains lower than that for atoms. Thus we can conclude that the most significant contribution to the total thermal conductivity of N_2/N and O/O_2 mixtures is given by atoms.

Fig. 1b presents the total coefficient of thermal conductivity λ' calculated as a function of x_a at fixed temperatures: in the mixture N_2/N $T = 22000$ K, and in the mixture O_2/O $T = 24000$ K. Fixed values of temperature correspond to the maxima of the atomic specific heats. The thermal conductivity coefficients increase significantly with the rise of atomic species. This confirms our conclusion that the most important contribution to the thermal conductivity coefficients is given by atoms, and the main role belongs to the atomic electronic states.

The coefficient of shear viscosity η for the N_2/N and O_2/O mixtures is given in Fig. 2 as a function of T and x_a . The shear viscosity increases with the temperature. For 70–80% fraction of atomic component in the mixture one can see a maximum for the shear viscosity coefficient.

Fig. 3 presents the coefficient of bulk viscosity ζ as a function of T and x_a . With the rise of T , the bulk viscosity coefficient behaves non-monotonically; for molecules, the bulk viscosity coefficient remains lower than that for atoms. This is explained by the fact that the relaxation time of molecular internal energy is less than that for atoms; the

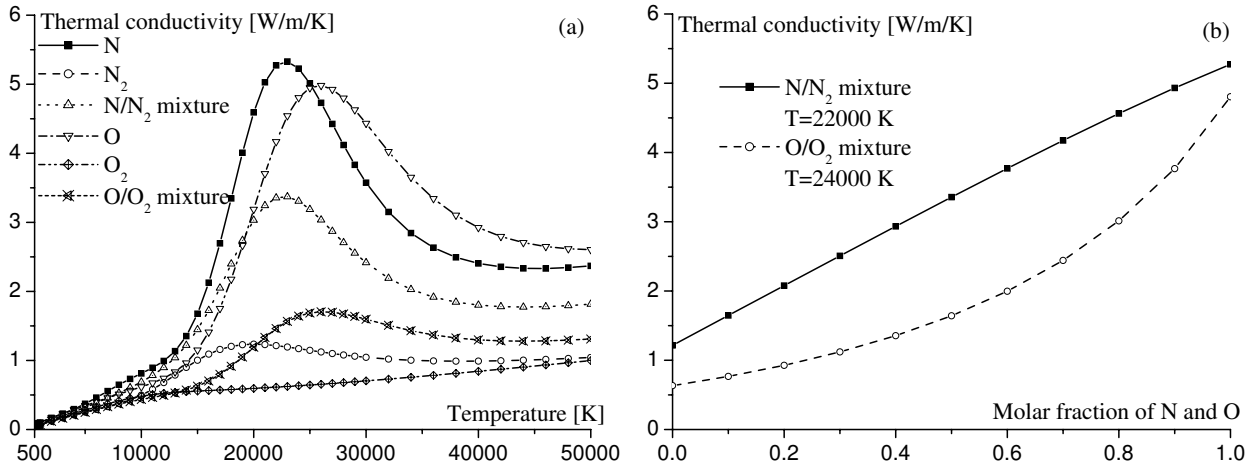


FIGURE 1. Thermal conductivity coefficient λ' as a function of T (a) and n_c (b).

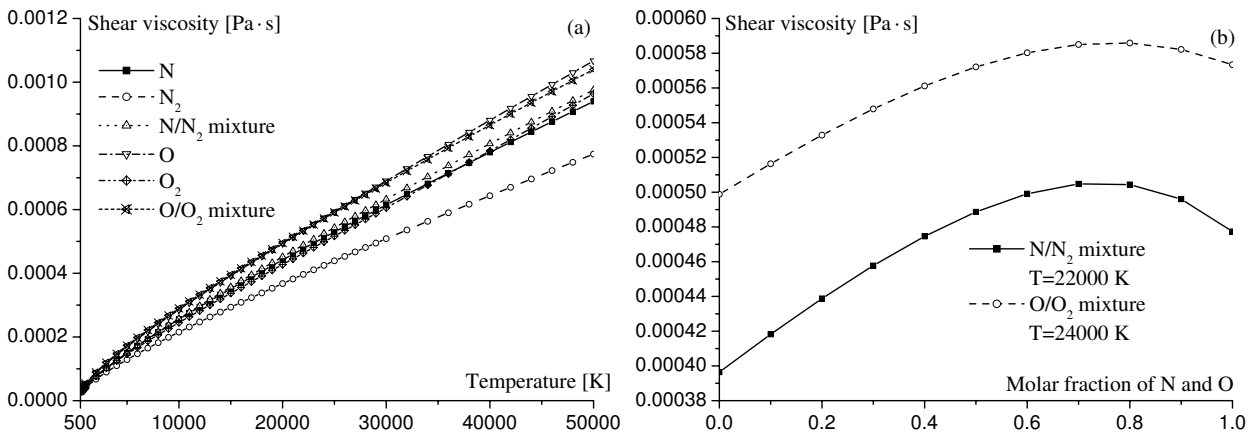


FIGURE 2. Shear viscosity coefficient η as a functions of T (a) and n_c (b).

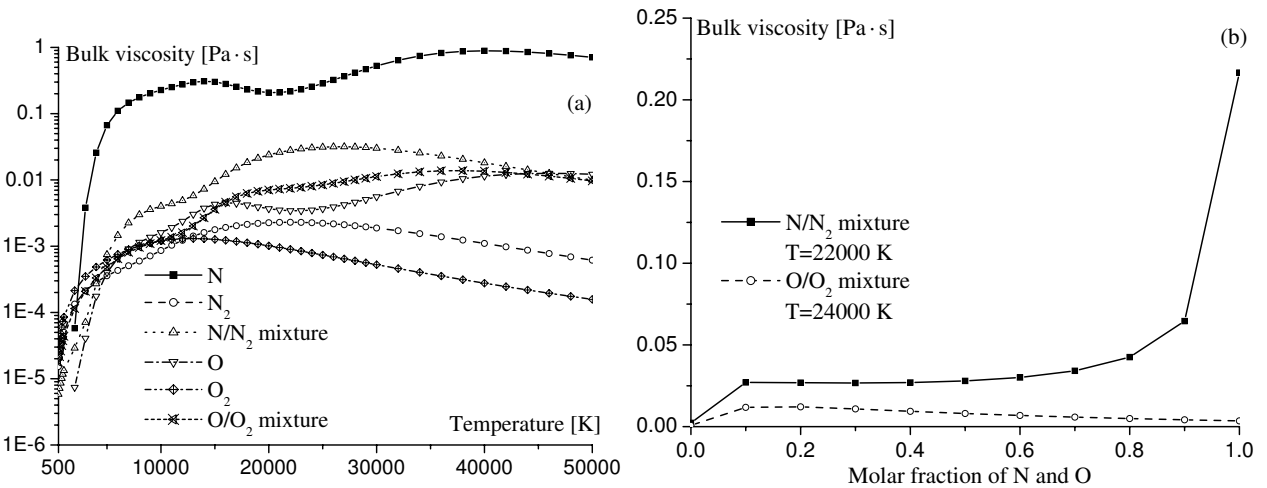


FIGURE 3. Bulk viscosity coefficient ζ as a functions of T (a) and n_c (b).

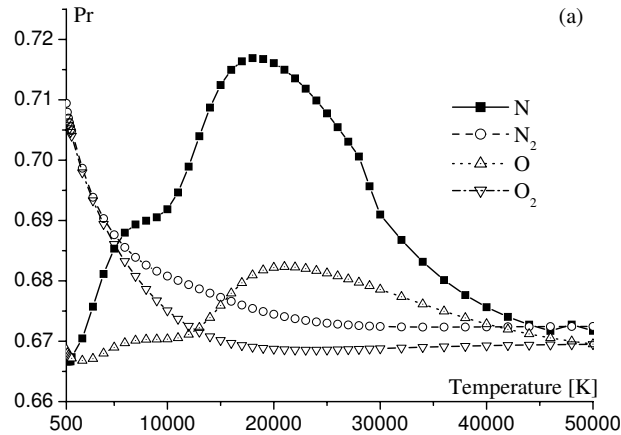


FIGURE 4. Prandtl number as a function of T .

discrepancy in the values of ζ for atoms is connected to the difference in the electronic deactivation rate constants. For N_2/N mixture, the bulk viscosity increases with the rise of the atomic molar fraction in the mixture. For the O_2/O mixture, we obtain the reversed situation: the maximum of the bulk viscosity value is achieved for the 10–30 % of atomic component in the mixture.

In Fig. 4, the Prandtl number

$$\text{Pr} = \frac{c_p \eta}{\lambda'} \quad (17)$$

is given as a function of T for different species. As can be seen, the Prandtl number of atomic and molecular components depends on T . The Prandtl number for N achieves the maximum in the temperature range $T = 18000 - 20000$ K with the value 0.72.

CONCLUSION

Theoretical model of transport properties in mixtures of dissociating nitrogen and oxygen with electronic excitation of atoms and molecules is developed. The contribution of electronic degrees of freedom to thermal conductivity, bulk viscosity and Prandtl number is found to be important. For atomic species, electronic excitation plays the most important role in the temperature range 20000–30000 K, where electronic thermal conductivity exceeds substantially the translational one. Further improvement of the model requires taking into account ionization processes.

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