ORIGINAL PAPER

Influence of the Excited States of Atomic Nitrogen N(^{2}D) and N(^{2}P) on the Transport Properties of Nitrogen. Part I: Atomic Nitrogen Properties

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Abstract In this paper, calculated values of the viscosity and thermal conductivity of atomic nitrogen, taking into account three species (the ground and two excited states), are presented. The calculations, which assume that the temperature dependent probability of occupation of the states is given by the Boltzmann factor, are performed for atmospheric-pressure in the temperature range from 1,000 to 20,000 K. Six collision integrals are used in calculating the transport coefficients and we have introduced new averaged collision integrals where the weight associated at each interacting species pair is the probable collision frequency. The influence of the collision integral values and energy transfer between two different species is studied. These results are compared which those of published theoretical studies.

1 Introduction

The knowledge of transport properties of atomic nitrogen (N) at high temperatures in air is important for creation of spacecrafts (upper atmosphere) [1] and for many applications [2, 3]. However results corresponding to this type of data are sparse and their values are scattered [4–6].

The theoretical prediction of transport properties requires the knowledge of potential energy curves which describe the interaction of different species. However many tables giving these coefficients are based on either incomplete data or their credibility is questionable. For example, some unknown potentials are often estimated with the help of crude physical models.

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Moreover, transport properties tables are established under the following assumption: to treat an atom—atom collision, the potentials of diatomic molecules taken into account are only those leading to a dissociation on the ground state of two atoms. For example, for the N–N collision, only four interaction potentials, for N_2, are generally retained: those leading to $N(^4S) + N(^4S)$. However, when the temperature increases, the excited states of atomic nitrogen ($N(^2D)$ and $N(^2P)$) having lowest energies populate. The aim of this paper is to relate the transport properties of atomic nitrogen within these excited states present.

In the first part of the paper, the composition is calculated and then the different potentials permitting to describe collisions between excited (or not) atoms of nitrogen are determined. The second part is devoted to transport properties, on one hand those obtained by taking into account only the collision $N(^4S)$–$N(^4S)$ and on the other hand those calculated by considering the three species of atomic nitrogen ($N(^4S)$, $N(^2D)$ and $N(^2P)$). Finally, we highlight the influence of energy transfers during a collision $N + N^*$ and we test the influence of transfer cross sections on the transport properties.

2 Composition

Our chemical system is composed of only three atomic species: $N(^4S)$, $N(^2D)$ and $N(^2P)$. The composition is calculated assuming that the probability of occupation of these states is given by Boltzmann factor. For a perfect gas, the total density n_t is given by $p = n_t \cdot k \cdot T$ with p, k and T are the pressure, the Boltzmann's constant and the temperature respectively. Moreover we have introduced, to determine the number density of the three species, a reduced partition function given by

$$Q(T) = \sum_{i=1}^{3} g_i \exp\left(-\frac{E_i}{T}\right) \tag{1}$$

where g_i and E_i are respectively the statistical weight and the energy of the ith state (see Table 1).

Figure 1 shows the evolution with temperature, at $p = 1$ atm, of the density of the three states noted N(4S), N(2D) and N(2P) but also the total density.

For $p = 1$ atm, the dissociation reaction of N_2 occurs for T_D # 8,000 K. At this temperature, for the number density of these three species ($n(^4S)$, $n(^2D)$ and $n(^2P)$) we have $n(^4S)$ # 13 $n(^2D)$ # 120 $n(^2P)$. Moreover the interaction N–N is significant up to 11,000 K, for this temperature we have $n(^4S)$ # 4.9 $n(^2D)$ # 28 $n(^2P)$. But by increasing the pressure, we shift the dissociation reaction towards high temperatures. For $p = 10$ atm and T # 13,000 K (T_D # 10,000 K) we have $n(^4S)$ # 3.4 $n(^2D)$ # 16 $n(^2P)$.

Table 1 Values of statistical weight and energy level for different states of N

States	N(^4S)	N(^2D)	N(^2P)
Statistical weight	4	10	6
Energy level	0	2.3839	3.5756
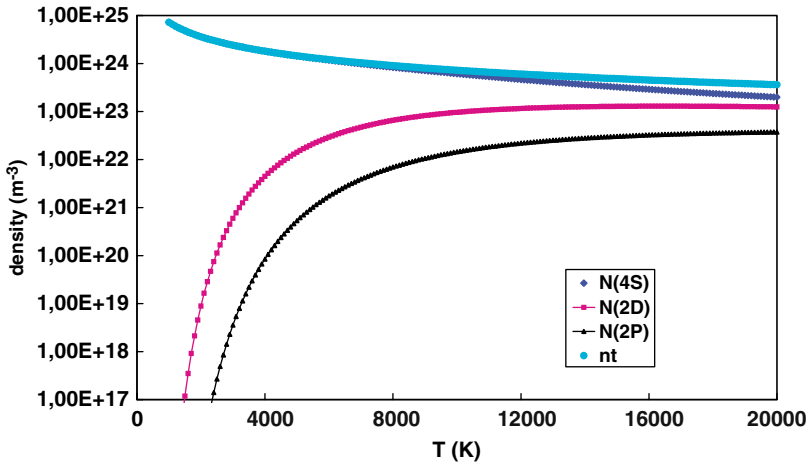
Fig. 1 Evolution of density versus temperature

3 Method to Calculate Transport Properties

From the Chapman–Enskog theory established [7] to determine transport properties of dilute gases, we have calculated the translational κ_{tr}, internal κ_{int} and reaction κ_{reac} thermal conductivities and the viscosity (noted vis or μ). Two cases have been studied:

– three species have been retained to determine the transport coefficients and in this first approach the total thermal conductivity must be written as $\kappa_t = \kappa + \kappa_{reac}$ with $\kappa_{int} = 0$.
– only one specie is taken into account with number density of n_t. In this second approach the transport properties are calculated as for a pure gas and the thermal conductivity must be written as $\kappa_t = \kappa_{tr} + \kappa_{int}$ with $\kappa_{reac} = 0$. Note that the basic formalism to determine the internal and reaction thermal conductivities is the same; the heat flux vector is written as:

$$\vec{q}_1 = \sum n_i h_i \overline{\vec{V}_i} = -\lambda_{reac} \nabla T = -\lambda_{int} \nabla T, \tag{2}$$

where h_i is the enthalpy associated to the specie i (for the reaction thermal conductivity) or at a particular quantum state (i) of the specie (for the internal thermal conductivity) and $\vec{V}_i$ is the diffusion velocity defined by

$$\overline{\vec{V}_i} = \frac{n_t}{n_i \rho k T} \sum_j m_j D_{ij} \vec{d}_j - \frac{D_i^T}{n_i m_i} \nabla(\ln T) \tag{3}$$

where T and ρ are respectively temperature and mass density of the mixture; n_j and m_j are respectively the number density and mass of the jth specie; D_{ij} and D_i^T are respectively ordinary and thermal diffusion coefficients. The term in $\vec{d}_j$ describes the diffusion forces due to gradients in concentration and pressure. When there are no gradients in pressure and external force, $\vec{d}_j = n_t k T \nabla x_i$; moreover by neglecting the

thermal diffusion coefficient in comparison with ordinary coefficient, relation (3) can be written as:

$$\overline{\overline{V}}_i = \frac{n_t^2}{n_i \rho} \sum_{j \neq i} m_i D_{ij} \nabla x_j \quad (D_{ii} = 0 \text{ by definition}) \tag{4}$$

By assuming that the molar fractions are function only of the temperature, we may write:

$$\nabla x_j = \frac{\mathrm{d} x_i}{\mathrm{d} T} \nabla T \tag{5}$$

and then to determine the internal or reaction thermal conductivities by solving the system (2).

But to obtain the actually proposed formalism for κ_{int}, another assumption is done: the diffusion coefficient is the same for all the quantum states and we introduce the binary diffusion coefficient $\mathcal{D}_{ii}$ which is nonzero (it is obtained by written for a single component the coefficient of diffusion of a binary mixture developed in the first approximation).

All these transport coefficients may be expressed with collision integrals given by

$$Q_{i,j}^{(\ell,s)} = \frac{4(\ell+1)}{(s+1)!(2\ell+1-(-1)^{\ell})} \int_0^{+\infty} e^{-\gamma^2} \gamma^{2s+3} Q_{i,j}^{(\ell)} \mathrm{d}\gamma \tag{6}$$

where γ^2 is a reduced energy, i and j represent the nature of interacting species, the values of the two superscripts ℓ and s depend of the approximation order retained, in our case we have $\ell_{\max} = 3$ and $s_{\max} = 5$. Finally, $Q_{i,j}^{(\ell)}$ is the transport cross section (as an example $\ell = 1$ for the diffusion cross section) depending on the interaction potential between two colliding particles.

At first the collision N(^{4}S)–N(^{4}S) and then five other collisions (N(^{4}S)–N(^{2}D) as an example) have been studied.

3.1 Collision N(^{4}S)–N(^{4}S)

When two ground state (^{4}S) N atoms encounter, the interaction may follow four potential curves corresponding to four electronic states of N$_2$: the ground $X^1\Sigma_g^+$ state and the three excited $A^3\Sigma_u^+$, and $^7\Sigma_u^+$ states. We have studied this collision previously [8] and we have determined averaged collision integrals for these four potentials:

$$\overline{Q}_{\text{SS}}^{(\ell,s)} = \sum_i \alpha_{\text{SS},i} \overline{Q}_{\text{SS},i}^{(\ell,s)} \tag{7}$$

where i represents the sum over the electronic states. The symbol $\alpha_{\text{SS},i}$ represents the probability associated with each electronic state $X^1\Sigma_g^+$, $A^3\Sigma_u^+$, and $(^7\Sigma_u^+)$ which is the degeneracy of each state (1, 3, 5 and 7 respectively) divided by the total degeneracy (16) of the electronic states.

Starting from these average collision integrals (Eq. 7), we may calculate the transport properties (second approach): κ_{tr} (SS), κ_{int} (SS), κ_t(SS) and vis(SS), in this case atomic nitrogen is considered as a pure gas.

In Fig. 2, we compare our values of collision integral $\overline{Q}_{SS}^{(1,1)}$, versus temperature, with those obtained by Levin et al. [9] and Rainwater et al. [10].

Our results are in good agreement with those obtained by these two authors and our values are between theirs. The largest discrepancy is obtained at 1,000 K: the collision integral values are respectively 20.29×10^{-20} m^2 for Rainwater et al. [10], 19.64×10^{-20} m^2 for us and 18.73×10^{-20} m^2 for Levin et al. [9]. For $T > 4,000$ K, the relative difference is lower than 1%.

3.2 Others Collisions

Now we have to study five collisions: N(^{4}S)–N(^{2}D), N(^{4}S)–N(^{2}P), N(^{2}D)–N(^{2}D), N(^{2}D)–N(^{2}P) and N(^{2}P)–N(^{2}P). The Table 2 shows all interaction potentials for these collisions, those for which we have data but also those for which we have no data.

For $B^3\Pi_g$, $B'^3\Sigma_u^-$, $a'^1\Sigma_u^-$, $a^1\Pi_g$, $w^1\Delta_u$, $H^3\Phi_u$ and $yE^3\Sigma_g^+$ states of N$_2$, we have retained the spectroscopic data of Hubert and Herzberg [11] and Loftus and Krupenie [12].

For $b'^1\Sigma_u^+$ state, same references are used however we have to homogenize the dissociation energies of N$_2$: the value reported by Loftus is overestimated approximately by 700 cm^{-1}.

For $W^3\Delta_u$ and $G^3\Delta_g$ states whose spectroscopic data are also available [11], for the first we have preferred the results of Cerny et al. [13] and for the second we have taken into account the dissociation energy of Phair et al. [14].

In theory, $C^3\Pi_u$ and $C'^3\Pi_u$ states should dissociate in N(^{4}S)–N(^{2}P) and N(^{4}S)–N(^{2}D) respectively. However, it is assumed that these two states dissociate to N(^{4}S)–N(^{2}D) due to interactions between them [15]. This assumption leads to a total
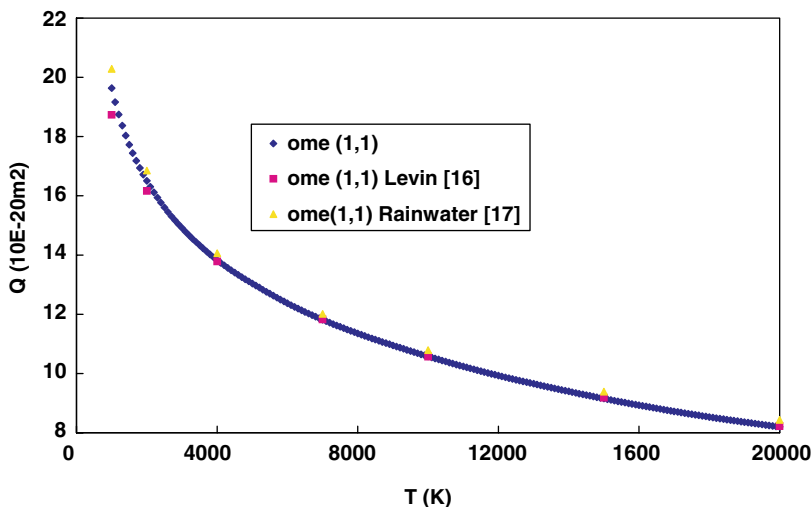

Fig. 2 Comparison of collision integrals versus temperature

Table 2 Interaction potentials and respective weights

Collisions	Known potentials	Weights	Unknown potentials	Weights
N(^{4}S)–N(^{2}D)	$B^3\Pi_g$, $W^3\Delta_u$, $G^3\Delta_g$	6, 6, 6	$^3\Sigma_u$, $^5\Sigma_{u,g}$, $^5\Pi_{u,g}$, $^5\Delta_{u,g}$	3, 10, 20, 20
	$C^3\Pi_u$, $C'^{\,3}\Pi_u$, $yE^3\Sigma_g^+$	6, 6, 3		
N(^{4}S)–N(^{2}P)	$B'^3\Sigma_u^-$	3	$^3\Sigma_g$, $^5\Sigma_{u,g}$, $^3\Pi_g$, $^5\Pi_{u,g}$	3, 10, 6, 20
N(^{2}D)–N(^{2}D)	$a'^1\Sigma_u^-$, $a^1\Pi_g$, $w^1\Delta_u$	1, 2, 2	$^1\Sigma_u^-$, $^1\Sigma_g^+(3)$, $^3\Sigma_g^-(2)$, $^3\Sigma_u^+(3)$	1, 3, 6, 9
	$H^3\Phi_u$	6	$^1\Pi_u$, $^3\Pi_g(2)$, $^1\Pi_u(2)$, $^3\Pi_u(2)$	2, 12, 4, 12
			$^1\Delta_g(2)$, $^3\Delta_g$, $^3\Delta_u(2)$	4, 6, 12
			$^1\Phi_{u,g}$, $^3\Phi_g$, $^1\Gamma_g$, $^3\Gamma_u$	4, 6, 2, 6
N(^{2}D)–N(^{2}P)	$b'^1\Sigma_u^+$	1	$^1\Sigma_g^+$, $^3\Sigma_{u,g}^+$, $^1\Sigma_{u,g}^-(2)$, $^3\Sigma_{u,g}^-(2)$	1, 6, 4, 12
			$^1\Pi_{u,g}(3)$, $^3\Pi_{u,g}(3)$, $^1\Delta_{u,g}(2)$	12, 36, 8
			$^3\Delta_{u,g}(2)$, $^1\Phi_{u,g}$, $^3\Phi_{u,g}$	24, 4, 12
N(^{2}P)–N(^{2}P)			$^1\Sigma_g(2)$, $^3\Sigma_g$, $^3\Sigma_u(2)$, $^1\Sigma_u$	2, 3, 6, 1
			$^1\Pi_g$, $^3\Pi_g$, $^1\Pi_u$, $^3\Pi_u$, $^1\Delta_g$, $^3\Delta_u$	2, 6, 2, 6, 2, 6

weight of 86 for the dissociation on N(^{4}S)–N(^{2}D) (instead of 80 allowed by the theory) and of 42 for the dissociation on N(^{4}S)–N(^{2}P) (instead of 48 allowed by the theory). For these two states, we have used the data of Huber and Herzberg [11] and Loftus and Krupenie [12] completed by those of Ledbetter [15].

The averaged collision integrals have been calculated, as for N(^{4}S)–N(^{4}S) collision (Eq. 7), taking into account only the known potentials: $\overline{Q}_{SD}^{(\ell,s)}$, $\overline{Q}_{SP}^{(\ell,s)}$, $\overline{Q}_{DD}^{(\ell,s)}$ and $\overline{Q}_{DP}^{(\ell,s)}$.

For the N(^{2}P)–N(^{2}P) collision, no data in the literature is found to best of our knowledge and hence we used the data of the N(^{2}D)–N(^{2}D) collision: $\overline{Q}_{PP}^{(\ell,s)} = \overline{Q}_{DD}^{(\ell,s)}$. This assumption is realistic due to the low density of N(^{2}P) independent of temperature as shown on Fig. 1.

With the help of six known average integral collisions $\overline{Q}_{SS}^{(\ell,s)}$, $\overline{Q}_{SD}^{(\ell,s)}$, $\overline{Q}_{SP}^{(\ell,s)}$, $\overline{Q}_{DD}^{(\ell,s)}$, $\overline{Q}_{DP}^{(\ell,s)}$ and $\overline{Q}_{PP}^{(\ell,s)}$ we may determine the transport properties (first approach) $\kappa_{tr}(SDP)$, $\kappa_{reac}(SDP)$, $\kappa_t(SDP)$ and vis(SDP) taking into account three species N(^{4}S), N(^{2}D) and N(^{2}P).

3.3 New Averaged Collision Integrals

At high temperature, collisions between excited electronic states or between the ground state and an excited electronic state may occur. Starting from the work of Biolsi and Holland [16], we have introduced new averaged collision integrals. We introduce the probability α_{ij} associated with two interacting species i and j (i, j = S, D or P for N(^{4}S), N(^{2}D) or N(^{2}P) respectively) as $\alpha = \frac{n(i)}{n_t} \times \frac{n(j)}{n_t}$ (independent

Table 3 Probability associated to interacting atoms

Interacting atoms	Probability associated
N(^{4}S)–N(^{2}D)	$\alpha_{SD} = 2g_1 g_2 \exp(-E_2/T)/Q^2$
N(^{4}S)–N(^{2}P)	$\alpha_{SP} = 2g_1 g_3 \exp(-E_3/T)/Q^2$
N(^{2}D)–N(^{2}D)	$\alpha_{DD} = g_2 g_2 \exp(-(E_2 + E_2)/T)/Q^2$
N(^{2}D)–N(^{2}P)	$\alpha_{DP} = 2g_2 g_3 \exp(-(E_2 + E_3)/T)/Q^2$
N(^{2}P)–N(^{2}P)	$\alpha_{PP} = g_3 g_3 \exp(-(E_3 + E_3)/T)/Q^2$

probability hypothesis). Under this assumption α_{ij}, for N(^{4}S)–N(^{4}S) collision, may be written as $\alpha_{SS} = \frac{g_1^2}{Q^2}$. The other probabilities are given in Table 3.

Finally, we have determined an averaged collision integral as:

$$\overline{Q}_f^{(\ell,s)} = \sum_{\substack{i,j \\ i \neq j}}^{3} \alpha_{ij} \overline{Q}_{ij}^{(\ell,s)} \tag{8}$$

Then the transport properties are calculated using the second approach for the transport properties: $\kappa_{tr}(wgh)$, $\kappa_{int}(wgh)$, $\kappa_t(wgh)$ and vis(wgh).

4 Results

At first, to test the validity of the two approaches, we introduce the same value for all averaged collision integrals $\overline{Q}_{SS}^{(\ell,s)} = \overline{Q}_{SD}^{(\ell,s)} = \overline{Q}_{SP}^{(\ell,s)} = \overline{Q}_{DD}^{(\ell,s)} = \overline{Q}_{DP}^{(\ell,s)} = \overline{Q}_{PP}^{(\ell,s)}$ in the computer code. And we verify, as previous by theory, that $\kappa_{tr}(SS) = \kappa(SPD) = \kappa_{tr}(wgh)$ (we have the same results for viscosity) which are quite reasonable but more important than $\kappa_{reac}(SPD) = \kappa_{int}(SS) = \kappa_{int}(wgh)$. We explain the small discrepancy (few per cent) by the approximation order retained: second order for κ_{reac} and first order for κ_{int}.

For the first approach, Fig. 3 depicts the dependence on temperature of the total thermal conductivity, but also these two components: reaction and total translational ($\kappa_{tr}(SDP)$) and finally the translational thermal conductivity associated with each specie ($\kappa_{tr}(^4S)$, $\kappa_{tr}(^2D)$ and $\kappa_{tr}(^2P)$ with $\kappa_{tr}(SDP) = \kappa(^4S) + \kappa_{tr}(^2D) + \kappa_{tr}(^2P)$) of N.

The maximum of the reaction thermal conductivity is observed at 13,600 K and its relative contribution to total thermal conductivity is then around 25%. The contribution of each state at the general translational thermal conductivity may be
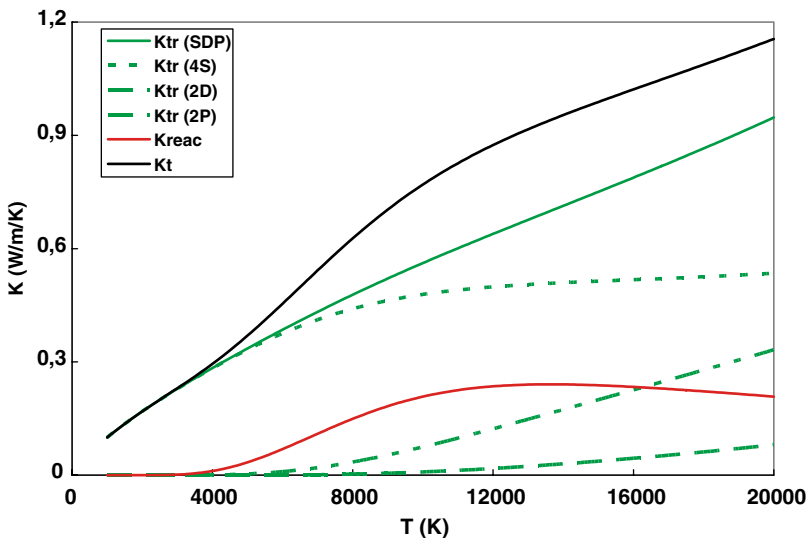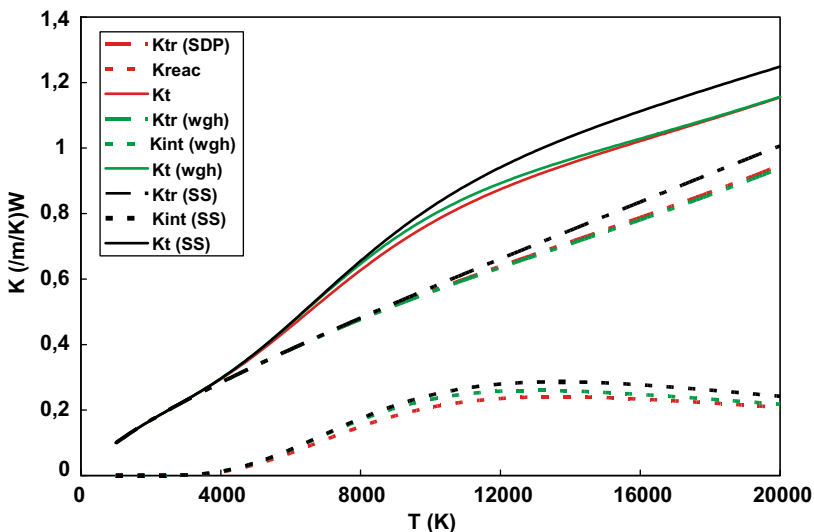

Fig. 3 Dependence on temperature of thermal conductivities

determined. For $T < 8,000$ K we have $\kappa_{tr}(SDP)$ # $\kappa_{tr}(^4S)$ but with temperature increasing the two other species are more and more involved and at $T = 20,000$ K the relative contributions to $\kappa_{tr}(SDP)$ are $\kappa(^4S) = 56$ %, $\kappa_{tr}(^2D) = 35$ % and $\kappa_{tr}(^2P) = 9$ %.

Classically, transport properties take into account only the ^4S–^4S collision. This assumption becomes less and less realistic when the temperature increases but is it really important? Then we have compared these results with those obtained under pure gas assumption. These calculations are performed using averaged collision integrals given respectively by relations (7) and (8). Figure 4 shows the evolution, versus temperature, of thermal conductivities. For the first approach we have the same notation than in the Fig. 1. For the second approach, we represent the total, translational and internal conductivities noted $\kappa_t(SS)$, $\kappa_{tr}(SS)$ and $\kappa_{int}(SS)$ (in this case the collision integrals are calculated from relation (7)) and $\kappa_t(wgh)$, $\kappa_{tr}(wgh)$ and $\kappa_{int}(wgh)$ (in this case the collision integrals are calculated from relation (8)).

Up to 10,000 K, there is good agreement between the different components of the thermal conductivity and the total thermal conductivity independent of the approach applied.

However, with temperature increasing, discrepancy appears between $\kappa_t(SS)$ and the two others total thermal conductivities : the collision integrals for only ^4S–^4S interaction are lower than those obtained for N-N* interaction (ground–excited state) leading to an increasing of $\overline{Q}_f^{(l,s)}$ (Eq. 8). At 20,000 K, we have $\kappa_t(SS) = 1.249$ W/m/K to compare with $\kappa_t(SDP) = 1.155$ W/m/K and $\kappa_t(wgh) = 1.157$ W/m/K: the relative discrepancy between the first thermal conductivity and the two others is around 9%. Moreover the total thermal conductivity is calculated by taking into account three species or with the second approach by introducing averaged collision integrals (Eq. 8) leads to the same results (relative discrepancy is around 0.1% at 20,000 K). This agreement is possible only due to the fact that κ_{reac} # $\kappa_{int}(wgh)$, the difference is introduced by collision integrals.

Fig. 4 Dependence on temperature of thermal conductivities
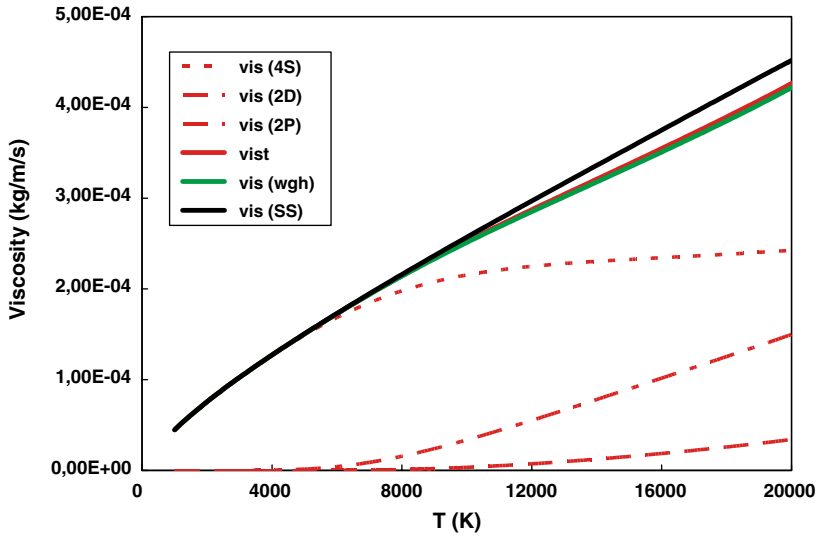
Fig. 5 Dependence on temperature of viscosities

Figure 5 shows the evolution versus temperature of the viscosities obtained with the second approach: $\mu(SS)$ and $\mu(wgh)$ (collision integrals obtained respectively with Eqs. 7 and 8) and with the first approach: μ_t (noted vist on Fig. 5). In this last case we represent also the contribution of the three states respectively: $\mu(S)$, $\mu(D)$ and $\mu(P)$ with $\mu_t = \mu(S) + \mu(D) + \mu(P)$.

The same comments as for Figs. 3 and 4 may be done. At $T = 20{,}000$ K, the relative contributions, for the three states, to the total viscosity are respectively $\mu(S) = 57\%$, $\mu(D) = 35\%$ and $\mu(P) = 8\%$. Moreover we have μ_t # $\mu(wgh)$ whatever the temperature and at $T = 20{,}000$ K we have $\mu(SS)/\mu t = 1.06$.

To conclude, at atmospheric pressure and in pure nitrogen, the dissociation of nitrogen occurs at T # $8{,}000$ K. When the difference between the values of the transport properties calculated with the two approaches becomes significant (for $T \geq 10{,}000$ K), ionization reaction occurs and the more significant interaction is N–N$^+$. In this case the assumption of a single collision (^{4}S–^{4}S) remains realistic if our collision integrals for the others interactions are accurate.

However it is well known that the dissociation and ionization reactions are shifted to higher temperatures as the pressure increases that may infirmed the previous conclusion. Moreover, the collision integrals are calculated:

(a) for the five interactions between ground state–excited state and excited state–excited state, from a few number of interaction potentials (see Table 2). Therefore, we have only an estimation of their values.

(b) without taking into account energy transfer during the N(^{4}S)–N(^{2}D) collision as an example.

And then we tested the influence on one hand of values of the collision integrals and an other hand of energy transfer between the different species.

4.1 Influence of the Collision Integral Values

To test the influence of the collision integral values, we have multiplied by 1.3 or 0.7 $\overline{Q}_{SD}^{(\ell,s)}, \overline{Q}_{SP}^{(\ell,s)}, \overline{Q}_{DD}^{(\ell,s)}, \overline{Q}_{DP}^{(\ell,s)}$ and $\overline{Q}_{PP}^{(\ell,s)}$ to underestimate or overestimate the values of transport properties.

The Figs. 6 and 7 represent respectively the translational thermal conductivity and viscosity as a function of temperature. In Fig. 6, the notation 1.0 indicates that the calculations are done without modified collision integrals, $\kappa_{tr}(1.3)$ and $\kappa_{tr}(0.7)$ are obtained with the first approach with modified collision integrals (multiplied by 1.3 or 0.7 respectively) and κ_{tr}(Biolsi) represents Biolsi data [16]. In Fig. 7, same kinds of notation are used.

We find that our results are in good agreement with those of Biolsi and Holland [16] for the thermal conductivity as for the viscosity. For the translational thermal conductivity we have, for $T = 20,000$ K, $\kappa_{tr}(1.3) = 0.785$ W/m/K and $\kappa(1.0) = 0.947$ W/m/K that leads to a relative discrepancy of 21% compared to an increase of 30% in the values of the collision integrals. The same kind of results is obtained for viscosity.

4.2 Influence of Energy Transfer

As shown in Fig. 1, at low temperatures only the ground state is significantly populated but with temperature increasing, the two lowest excited states populate also. Then the excitation exchange process may occur as the following reaction:

$$N + N^* \rightarrow N^* + N$$
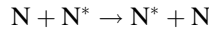
As for charge transfer, the collision integrals for this interaction are much greater than those obtained classically with the interaction potentials (for ℓ odd). In this
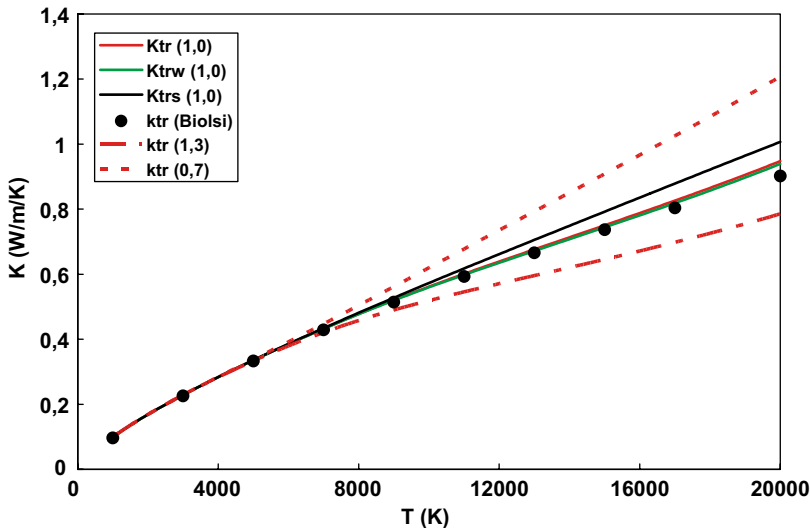
Fig. 6 Evolution of the translational thermal conductivity with temperature (notation given in the text)
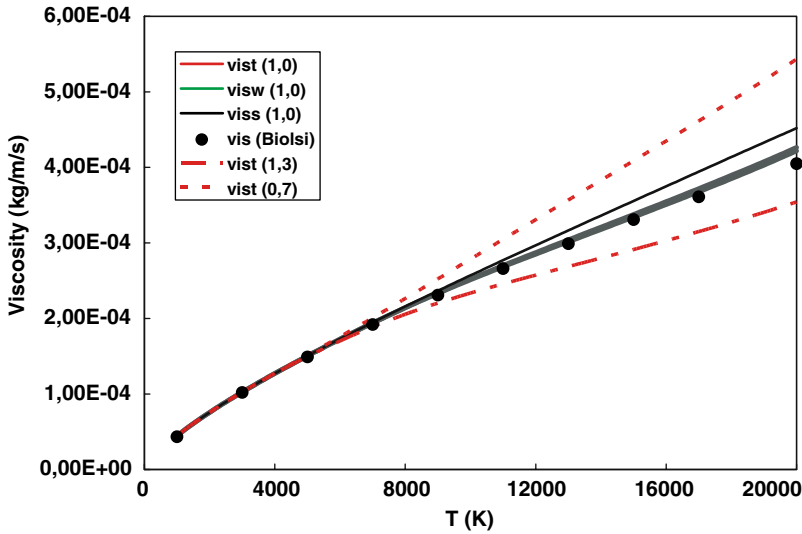
Fig. 7 Evolution of the viscosity with temperature (notation given in the text)

case, the atom–atom cross sections, when the atoms are in different electronic states, may be computed with a good approximation from the total cross sections for excitation exchange by the set of equations given elsewhere [17, 18] (as for charge transfer).

First, we have to fit the difference between each pair of gerade ($V_g^{(n)}$) –ungerade ($V_u^{(n)}$) potential energy curves to obtain two parameters $V_o^{(n)}$ and $\alpha^{(n)}$ (where n is relative to the nth pair of gerade–ungerade molecular state) through the following relation:

$$\left| V_g^{(n)} - V_u^{(n)} \right| = V_o^{(n)} \exp(-\alpha^{(n)} r) \tag{9}$$

Secondly, solving a transcendental equation, the dependence of the excitation transfer cross sections on the relative speed g is given by

$$Q_{ex}^{(n)} = \frac{1}{2}(A_n - B_n \ln g)^2 \tag{10}$$

where the constants A_n and B_n, characteristic of the nth gerade–ungerade pair, have been determined by least squares technique.

Finally $\overline{Q}_{tr}^{(\ell,s)}$ is obtained by the expression given by Devoto [19].

In our case, there are two possibilities to determine the energy transfers to the $N(^4S)$–$N(^2D)$ collision: $^3\pi_{u,g}$ and $^3\Delta_{u,g}$ (for the potentials $^3\Sigma$, $^6\Sigma$, $^5\pi$ and $^5\Delta$ we have not one or two potential curves). We have suppressed $^3\pi_{u,g}$ states because of crossing of potentials for $^3\pi_u$ states [12, 15]. Then we have retained only $^3\Delta$ molecular state. V_o and α coefficients are determined for $r \in [1, 3; 3, 2]$ Å, and we have obtained: $V_o = 283$ eV and $\alpha = 3.13$ Å^{-1} that leads to $A = 13.75$ Å and $B = 0.597$ Å.

Several years ago, Nyeland and Mason [17] calculated the excitation transfer cross sections for the $N(^4S)$–$N(^2D)$ and $N(^4S)$–$N(^2P)$ collisions. The necessary potential

curves are determined partly from spectroscopic data and partly from Heitler–London approximations. These values of $V_o^{(n)}$ and $\alpha^{(n)}$ are given for N(^{4}S)–N(^{2}D) interaction (six pairs of gerade–ungerade potential curves) and for N(^{4}S)–N(^{2}P) collision (four pairs) respectively in Tables 2 and 3 of their paper. Then we have calculated, for each pair, the excitation transfer cross sections $Q_{ex}^{(n)}$ but also $\overline{Q}_{tr}^{(\ell,s)}$, the averaged excitation transfer integral collisions are finally obtained with relation (7 or 8).

Figure 8 depicts the dependence on temperature of the different collision integrals for $\ell = 1$ and $s = 1$:

– Qtr(S,D) (Ny), Qtr(S,P) (Ny) and Qtr(S,D) (del,Ny) are calculated with Nyeland data and represent respectively the averaged collision integrals for N(^{4}S)–N(^{2}D) and N(^{4}S)–N(^{2}P) interactions and the last is obtained for $\Delta_{g,u}$ potential pair (N(^{4}S)–N(^{2}D) collision),
– Qtr(S,D) (del,ours) represents our results obtained for $\Delta_{g,u}$ potential pair (N(^{4}S)--N(^{2}D) collision).

The shapes of the four curves are the same. At $T = 10{,}000$ K and for $\ell = 1$ and $s = 1$, we have obtained Qtr(S,D) (del,ours) = 32.1 10^{-20} m^2 compared to Qtr(S,D) (Ny) = 21.8×10^{-20} m^2 and Qtr(S,P) (Ny) = 38.5×10^{-20} m^2.

Our values being between those obtained by Nyeland and Mason [17] for N(^{4}S)–N(^{2}D) and N(^{4}S)–N(^{2}P), to test the influence of the excitation transfer, we have used our data and admit that $\overline{Q}_{tr}^{(\ell,s)}(S,D) = \overline{Q}_{tr}^{(\ell,s)}(S,P) = \overline{Q}_{tr}^{(\ell,s)}(D,P) = $ Qtr(S,D)(del,ours) for the three averaged collision integrals for ℓ odd. For ℓ even, we have maintained the values calculated previously. With these modifications on the values of the collision integrals, the Fig. 9 depicts the different components of the thermal conductivity versus temperature (the same notations that those in the Figs.3 and 4 are used).
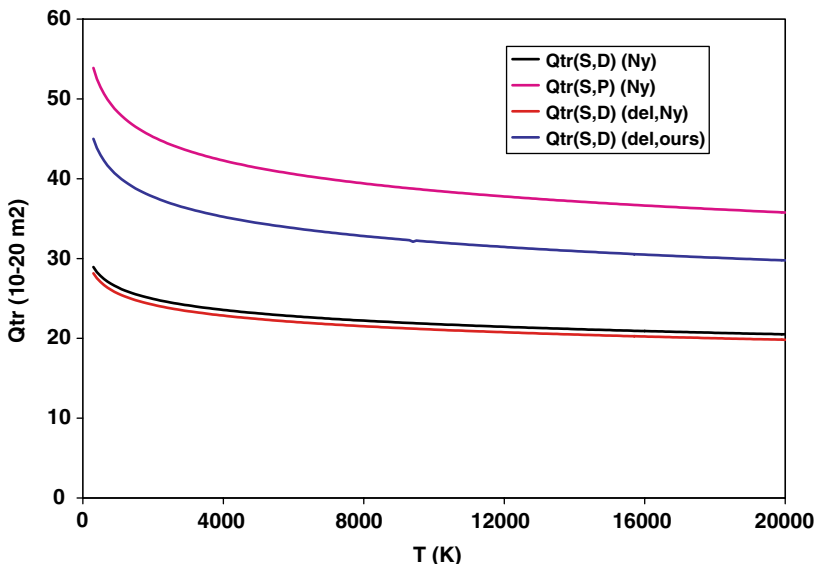
Fig. 8 Evolution of the integral collisions with temperature (notation given in the text)
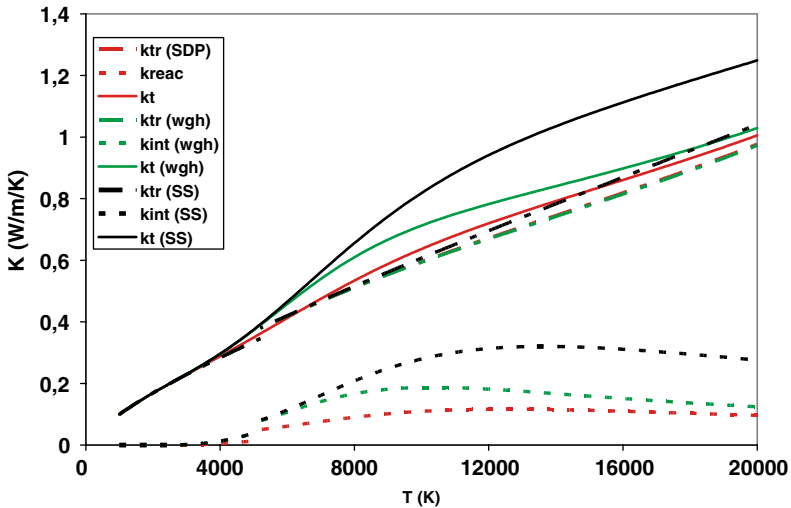
Fig. 9 Evolution of the different components of thermal conductivity with temperature

First, the introduction of excitation transfer collision integrals in the computer codes induces a small modification of the translational thermal conductivity and viscosity. We obtained, for those two transport properties, the same relative discrepancy. As an example we obtained, between κ_{tr}(SDP) calculated with and without excitation transfer, the maximum value at $T = 20,00$ K: 0.5%.

Second we have to compare κ_{reac}, κ_{int}(SS) and κ_{int}(wgh).

For a better understanding, we have taken into account, for the first approach (determination of κ_{reac}), only two states: the ground state (N(^{4}S)) and the first excited state (N(^{2}D)). In this particular case the composition reduces to a binary mixture (species are quoted respectively S and D for N(^{4}S) and N(^{2}D)). Then from Eqs. 4 and 5 it is easy to deduce, for the first approximation order: $\kappa_{reac} = f\left(\overline{Q}_{SD}^{(1,1)}\right)$ where $\overline{Q}_{SD}^{(1,1)}$ are the transfer excitation collision integrals. Moreover we have κ_{int}(SS) $= f\left(\overline{Q}_{SS}^{(1,1)}\right)$ where $\overline{Q}_{SS}^{(1,1)}$ is given by the relation (7).

In table 4, we have summarized ours results for different values of temperature. We give the values of κ_{reac} and κ_{int}(SS) in W/m/K, $\overline{Q}_{SD}^{(1,1)}$ and $\overline{Q}_{SS}^{(1,1)}$ in 10^{-20} m^2 and the products $\kappa_{reac} \times \overline{Q}_{SD}^{(1,1)}$ and κ_{int}(SS) $\times \overline{Q}_{SS}^{(1,1)}$.

Note that $\kappa_{reac} \times \overline{Q}^{(1,1)} \approx \kappa_{int}$(SS) $\times \overline{Q}_{SS}^{(1,1)}$ are similar as previous by theory at all temperatures. The discrepancy (the relative values are approximately of 1%) is

Table 4 Influence of the collision integrals on the thermal conductivity

T (K)	8,000	12,000	16,000	20,000
κ_{reac}	0.04998	0.06703	0.05983	0.04881
$\overline{Q}_{SD}^{(1,1)}$	32.82	31.45	30.50	29.77
$\kappa_{reac} \times \overline{Q}_{SD}^{(1,1)}$	1.64	2.11	1.82	1.45
κ_{int}(SS)	0.1425	0.2093	0.2015	0.1748
$\overline{Q}_{SS}^{(1,1)}$	11.35	9.929	8.930	8.197
κ_{int}(SS) $\times \overline{Q}_{SS}^{(1,1)}$	1.62	2.08	1.80	1.43

explained by the difference between the upper approximation order retained for the determination of κ_{reac} as previously remarks at the beginning of results part.

Then we worked with three states (including $N(^2P)$) and in Table 5 we present our results as in Table 4 but now we give also $\kappa_{\mathrm{int}}(\mathrm{wgh})$ in W/m/K, $\overline{Q}_{\mathrm{f}}^{(1,1)}$ in 10^{-20} m^2 (relation (8)) and the products $\kappa_{\mathrm{int}}(\mathrm{wgh}) \times \overline{Q}_{\mathrm{f}}^{(1,1)}$.

Remark that:

– as $\kappa_{\mathrm{int}}(\mathrm{wgh})$ and $\kappa_{\mathrm{int}}(\mathrm{SS})$, are calculated alike, the products are $\kappa_{\mathrm{int}}(\mathrm{wgh}) \times \overline{Q}_{\mathrm{f}}^{(1,1)}$ and $\kappa_{\mathrm{int}}(\mathrm{SS}) \times \overline{Q}^{(1,1)}$ almost exactly the same. But now $\kappa_{\mathrm{reac}} \times \overline{Q}_{\mathrm{SD}}^{(1,1)}$ is quite different (the relative discrepancy is around 5%): κ_{reac} is calculated at different approximation order but also its determination takes into account a lot of averaged collision integrals.
– for $12{,}000 < T < 20{,}000$ K, we have $\kappa_{\mathrm{int}}(\mathrm{SS}) - \kappa_{\mathrm{reac}} \approx 0.2$ W/m/K. The use of $\overline{Q}_{\mathrm{f}}^{(1,1)}$ to calculate κ_{int} improves the results, $\kappa_{\mathrm{int}}(\mathrm{wgh}) - \kappa_{\mathrm{reac}} \approx 0.079$ W/m/K (for $T = 8{,}000$ K) and goes down to 0.032 W/m/K at $T = 20{,}000$ K.
– from Tables 4 and 5, we may show the influence of $N(^2P)$ states on κ_{int}: the relative contribution is around 18% at $T = 8{,}000$ K and reach 28% at $T = 20{,}000$ K; it is only of 12 % at $T = 6{,}000$ K (out of tables).
– the ratio $R = \frac{\kappa_{\mathrm{t}}(\mathrm{SS}) - \kappa_{\mathrm{t}}}{\kappa_{\mathrm{t}}(\mathrm{SS})}$ is maximum at $T \approx 13{,}000$ K ($R = 24\%$) moreover $R = 19\%$ at $T = 8{,}000$ and 20,000 K.

5 Conclusions

To calculate transport properties we have to know the mixture composition and the collision integrals. In this paper we have only three species ($N(^4S)$ the ground state, $N(^2D)$ and $N(^2P)$ the two first excited states) and their densities are obtained assuming that the temperature dependent probability of occupation of the states is given by the Boltzmann factor.

After we have determined collision integrals:

– the $N(^4S)$–$N(^4S)$ collision has been studied previously [8] and our results for $\overline{Q}_{\mathrm{SS}}$ are in good agreement with those of Levin et al. [9] and Rainwater et al. [10],
– for the five others collisions, we take into account the same interaction potentials as Biolsi and Holland [16] but a lot of them are unknown ($\overline{Q}_{\mathrm{SD}}, \overline{Q}_{\mathrm{SP}}, \overline{Q}_{\mathrm{DD}}, \overline{Q}_{\mathrm{DP}}$ and $\overline{Q}_{\mathrm{PP}}$).

Table 5 Influence of the collision integrals on the thermal conductivity

T (K)	8,000	12,000	16,000	20,000
κ_{reac}	0.05711	0.08364	0.07688	0.06313
$\overline{Q}_{\mathrm{SD}}^{(1,1)}$	32.82	31.45	30.50	29.77
$\kappa_{\mathrm{reac}} \times \overline{Q}_{\mathrm{SD}}^{(1,1)}$	1.87	2.63	2.34	1.88
$\kappa_{\mathrm{int}}(\mathrm{wgh})$	0.1357	0.1540	0.1234	0.09545
$\overline{Q}_{\mathrm{f}}^{(1,1)}$	14.58	18.03	20.06	20.78
$\kappa_{\mathrm{int}}(\mathrm{wgh}) \times \overline{Q}_{\mathrm{f}}^{(1,1)}$	1.98	2.78	2.48	1.98
$\kappa_{\mathrm{int}}(\mathrm{SS})$	0.1742	0.2795	0.2771	0.2420
$\overline{Q}_{\mathrm{SS}}^{(1,1)}$	11.35	9.929	8.930	8.197
$\kappa_{\mathrm{int}}(\mathrm{SS}) \times \overline{Q}_{\mathrm{SS}}^{(1,1)}$	1.98	2.78	2.47	1.98

Finally, we have introduced new averaged collision integrals $\overline{Q}_f$ where the weight, associated at each interacting species pair, is probable collision frequency.

We have determined two transport properties: the viscosity and the thermal conductivity

– on one hand considering only one specie (the thermal conductivity reduce to its translational and internal parts) and we use $\overline{Q}_{SS}$ or $\overline{Q}$,
– on the other hand introducing three species and in the case we retain $\overline{Q}_{SS}, \ldots, \overline{Q}_{PP}$ (the thermal conductivity takes into account the translational and reaction parts).

With this set of collision integrals, the transport properties values are quite the same for all the temperatures. The maximum relative discrepancy is less than 1% (at 20,000 K) for thermal conductivity. Moreover, our results are in good agreement with those of Biolsi and Holland [16] for viscosity and translational thermal conductivity.

Finally we have tested the influence of the collision integral values and the excitation transfer during an interaction between two different species. These collision integrals are calculated as for charge transfer. We have used $\Delta_{u,g}$ potential pair and compared our results with those obtained starting from Nyeland works [17]. In this last case, we have shown that the translational thermal conductivity (but also the viscosity) are poorly modified by introducing excitation transfer collisions. Moreover, we have shown that $\kappa_{int}(SS)$ is, at least, three times larger than κ_{reac} whatever be the temperature between 8,000 and 20,000 K. However the use of $\overline{Q}_f$ to determine $\kappa_{int}(wgh)$ improves the results: $\kappa_{int}(wgh)/\kappa_{reac} = 2.4$ and 1.5, respectively at 8,000 and 20,000 K.

The part II of this paper is devoted to the determination of transport properties of nitrogen plasma. We shall calculate the composition taking into account:

– five species (e, N_2, N, N^+ and N_2^+),
– eight species (e, N_2, N(^{4}S), N(^{2}D), N(^{2}P), N(R), N^+ and N_2^+) where N(R) is fictitious specie constituted of all the others excited states of N.

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