Collision Integrals for Interactions Involving Atoms in Electronically Excited States[†]

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Transport collision integrals for low-lying excited states of nitrogen atoms and ions are derived in the framework of a phenomenological approach following, where possible, also the traditional multipotential procedure. The two sets of results are compared considering critically the observed deviations, and finally, the proposed model is validated by comparison with oxygen atom−atom interactions. In addition, an attempt is made to extend the proposed phenomenological method to interactions involving high-lying excited states, taking into account the symmetric interaction of two excited hydrogen atoms, characterized by increasing principal quantum number.

Introduction

The prediction of heat fluxes at the surface of a space vehicle during the (re)entry into the planetary atmosphere, relevant to the design of thermal protection systems, requires a reliable estimation of the transport properties of the plasma formed in the shock layer. Though extensive and accurate tabulations of transport coefficients (viscosity, thermal and electrical conductivity) for different atmospheres are nowadays available in the literature,[1−4] the excited-state issue still represents an open problem. In transport calculations, chemical species are usually regarded as being in the ground state; however, a deep investigation on the case of atomic hydrogen plasma in thermodynamic equilibrium[5,6] showed that transport coefficients are strongly affected by the presence of electronically excited atoms, especially in high-pressure regimes and under the action of an external magnetic field.[7]

Despite the relevance of the matter, only few examples attempting the derivation of collision integrals for interactions involving excited species are present in the literature. For air species—namely oxygen and nitrogen atoms and ions—the investigation was focused on the so-called *low-lying* excited states; that is, states sharing the same electronic configuration of the ground term.[8−11] Collision integrals have been estimated as the weighted average of different electronic states, considering also the contribution due to inelastic channels that affect the odd-order terms.[12,13] The dependence on electronic excitation of colliding partners was actually weak; however, the paper by Eletskii,[14] estimating the charge-exchange contribution in highly excited state interactions, demonstrated that greater effects are expected, increasing the principal quantum number.

For hydrogen, a database of transport cross sections has been created by using scaling relations or extrapolation formulas fitting available excited-state calculations.[15,16]

The derivation of complete and internally consistent data set of collision integrals for excited species is strongly hindered, within a traditional calculation scheme, by the need for accurate potential energy curves for the multiplicity of electronic terms correlating with species in a specific quantic state. This is already a challenging problem, since in the combination of orbital and spin angular momenta, a multiplicity of states arise, whose potential energy curves are largely unknown. Considering highly excited states ($n \gg 1$) the situation is even more complex, requiring new ab initio methods.

In this frame, the phenomenological approach, describing the global interaction and already validated in the case of ground-state interactions,[17] could be a highly desirable tool, overcoming the high computational cost of a multipotential approach.

In the present work, results are presented relative to the derivation, within the phenomenological approach, of elastic collision integrals for a nitrogen system in ground and low-lying states, including the inelastic contribution to the *l*-odd-term collision integrals; that is, diffusive-type $\sigma^2\Omega^{(1,1)*}$ due to the resonant charge/excitation exchange and obtained by using an asymptotic approach. The validation proceeds through the comparison of phenomenological viscosity-type collision integrals, not affected by inelastic processes, for interactions involving low-lying excited states for the O_2 system. Moreover, an attempt is made to describe the dependence on the principal quantum number of collision integrals for symmetric interactions in $H(n)-H(n)$ system, slightly modifying the potential function of the phenomenological method. In both cases, also, the customary multipotential procedure has been followed, including in the calculation the available electronic terms for validation purposes.

It should be noted that low-lying atomic states of both nitrogen and oxygen are important also at low pressure; that is, in reentry conditions. In this case, their populations are not in steady state with the ground state, thus requiring them to be transported as separate species with their own diffusive cross sections.

Interactions Involving Low-Lying Excited States

For N_2* and N_2^{+}* excited systems, only a few electronic terms are available, from ab initio calculations or from

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TABLE 1: Parameters of Hulburt-Hischfelder (Bound States) and Repulsive Potentials for Electronic Terms Relevant to $N(^4S)-N(^2D)$ and $N(^4S)-N^+(^1D)$ Interactions

interaction	term	α_{hh}	β_{hh}	γ_{hh}	ε_0 (eV)	r_e (Å)
$N(^4S)-N(^2D)$	$C'^3\Pi_u$	14.335	1784.254	17.011	0.090	1.515
	$E^3\Sigma_g^+$	13.818	−0.235	−223.456	0.403	1.118
	$C''^5\Pi_u$	3.027	2.755 (−03)	−1.475	0.588	1.450
	$C^3\Pi_u$	7.584	268.601	8.031	1.238	1.149
	$G^3\Delta_g$	3.646	4.424	−0.354	1.385	1.611
	$W^3\Delta_u$	3.123	3.053	2.784	4.874	1.280
	$B^3\Pi_g$	3.408	5.566	3.055	4.897	1.213
	$^5\Sigma_g^+$	7.319	1.671 (−02)	−3.354	0.303	2.130
		A (eV)	α_1^{rep} (Å^{-1})	α_2^{rep} (Å^{-2})		
	$^5\Pi_g$	43.886	0.679	0.723		
	$^5\Delta_g$	74.468	0.800	0.750		
$N(^4S)-N^+(^1D)$	$^4\Sigma_u^-$	3.184	2.603	6.881	4.073	1.390
	$^4\Delta_u$	2.716	2.241	5.584	4.925	1.410

TABLE 2: Parameters of Phenomenological Potential for Interactions Relevant to Atomic ($\alpha^{^4S}$ = 1.1 Å^3,[29] $\alpha^{^2D}$ = 1.1657 Å^3, $\alpha^{^2P}$ = 1.2232 Å^3,[30]) and Ionic ($\alpha^{^3P}$ = 0.55 Å^3,[29] $\alpha^{^1D}$ = 0.527 Å^3, $\alpha^{^1S}$ = 0.585 Å^3,[31]) Nitrogen in Low-Lying Excited States

interaction		ε_0 (meV)	r_e (Å)	β	m	interaction		ε_0 (meV)	r_e (Å)	β	m
$N(^4S)$	$N(^4S)$	6.432	3.583	6.605	6	$N^+(^3P)$	$N(^4S)$	94.581	2.956	6.759	4
	$N(^2D)$	6.550	3.598	6.802	6		$N(^2D)$	98.213	2.969	7.096	4
	$N(^2P)$	6.646	3.611	6.798	6		$N(^2P)$	101.31	2.981	7.088	4
$N(^2D)$						$N^+(^1D)$	$N(^4S)$	95.687	2.943	7.013	4
	$N(^2D)$	6.675	3.613	7.188	6		$N(^2D)$	99.344	2.957	7.717	4
	$N(^2P)$	6.777	3.625	7.178	6		$N(^2P)$	102.46	2.968	7.697	4
$N(^2P)$						$N^+(^1S)$	$N(^4S)$	93.006	2.975	7.007	4
	$N(^2P)$	6.884	3.638	7.169	6		$N(^2D)$	96.603	2.988	7.7006	4
							$N(^2P)$	99.670	2.999	7.6816	4

spectroscopic data models, reflecting the theoretical and experimental limits in studying excited states.

For $N(^4S)-N(^2D)$ interaction, a procedure is followed[18] that starting from the information on spectroscopic data of bound states (dissociation energy, equilibrium internuclear distance, fundamental frequency, anharmonic constant, ...) allows the derivation of parameters for the description of the corresponding potential energy curve with a Hulburt−Hirschfelder function (eq 1), depending on the depth (ε_0) and the position (r_e) of the potential well. Repulsive terms from ab initio calculations[19] are interpolated with a modified exponentially decaying function, eq 2, that accommodates the short-range potential behavior. Potential energy curves for bound electronic states of the N_2^+ molecular ion have been theoretically studied in the literature;[20] thus, for $N(^4S)-N^+(^1D)$ interaction, ab initio data are fitted by the Hulburt−Hirschfelder function. In Table 1, potential parameters relevant to the considered interactions are presented.

$$\varphi(r) = \varepsilon_0\{\exp[-2\alpha_{hh}x] - 2\exp[-\alpha_{hh}x] + \beta_{hh}x^3[1 + \gamma_{hh}x]\exp[-2\alpha_{hh}x]\} x = (r/r_e - 1) \quad (1)$$

$$\varphi(r) = A\exp(-\alpha_1^{rep}r - \alpha_2^{rep}r^2) \quad (2)$$

Elastic collision integrals result from a weighted averaging procedure, including the contribution of the available electronic terms that in the case of $N(^4S)-N(^2D)$ interaction are limited to 10 states out of the 13 theoretically predicted, whereas for $N(^4S)-N^+(^1D)$, the number of states is 2 out of 6.

We here propose an alternative estimation of the elastic contribution to collision integrals from the classical integration of a phenomenological potential, having the same functional form already adopted in describing the interactions between unexcited species.[17] This choice is justified by considering that low-lying excited states are characterized by physical properties quite similar to the ground state and by small energy separation.

The potential is modeled, considering the average interaction and resulting from the balance of attractive and repulsive terms[21−23]

$$\varphi = \varepsilon_0\left[\frac{m}{n(x) - m}\left(\frac{1}{x}\right)^{n(x)} - \frac{n(x)}{n(x) - m}\left(\frac{1}{x}\right)^{m}\right] \quad (3)$$

where $x = r/r_e$, $n(x) = \beta + 4x^2$. The first term represents the repulsion, and the second one, the attraction.

Potential features, such as the well depth and position, are derived by correlation formulas given in terms of fundamental physical properties of involved interacting partners (polarizability, α; charge; number of electrons effective in polarization).[24−28] The m parameter depends on the interaction type (4 for ion-neutral and 6 for neutral−neutral interactions, respectively), whereas a simple empirical formula based on polarizability of the colliding species has been proposed[17] for the estimation of the β parameter.

In Table 2, parameters of phenomenological potential for interactions relevant to atomic and ionic nitrogen excited states are reported and exhibit a regular trend governed by the increase in the polarizability corresponding to electronic excitation, with the exception of the β value, which is influenced by the change in the spin multiplicity of the excited states.

In ref 32, suitable bidimensional fitting expressions are given for reduced collision integrals, $\Omega^{(l,s)*}$ up to order (4, 4), over a wide range of reduced temperatures, allowing the estimation of a consistent and complete set of collision integrals on the base of the *tuplet* (r_e, ε_0, β, m), completely characterizing the physical system.

Table 3 presents values of the pure elastic diffusion-type component and of the viscosity-type collision integrals relevant to the first excited dissociation limit for N_2 and N_2^+

TABLE 3: Diffusion-Type (Elastic Contribution) and Viscosity-Type Collision Integrals (Å^2) Obtained by the Classical Approach, $\sigma^2\Omega_c^{(l,s)}$, and by the Phenomenological Approach, $\sigma^2\Omega_f^{(l,s)}$, as a Function of Temperature, for N(^{4}S)−N(^{2}D) and N(^4S)−N$^+$(^{1}D) Interactions

T (K)	$\sigma^2\Omega_f^{(1,1)*}$	$\sigma^2\Omega_f^{(2,2)*}$	$\sigma^2\Omega_c^{(1,1)*}$	$\sigma^2\Omega_c^{(2,2)*}$	$\sigma^2\Omega_c^{(2,2)*}$ [9]
			N(^{4}S)−N(^{2}D) Interaction		
1000	6.4412	7.4024	6.7096	7.0348	6.8684
2000	5.5564	6.4654	5.4625	5.8568	5.6967
4000	4.7676	5.6029	4.2661	4.6625	4.6980
6000	4.3435	5.1287	3.6548	4.0365	4.1260
9000	3.9461	4.6787	3.1168	3.4940	3.5547
10000	3.8473	4.5659	2.9867	3.3650	3.4099
20000	3.2420	3.8691	2.2067	2.5874	2.4890
			N(^{4}S)−N$^+$(^{1}D) Interaction		
1000	10.398	11.610	12.829	12.703	
2000	7.0621	7.8801	10.587	10.228	
4000	5.4095	6.1039	8.8556	8.3871	
6000	4.8021	5.4742	7.9346	7.5554	
9000	4.3217	4.9769	6.9365	6.8684	
10000	4.2102	4.8607	6.6465	6.6858	
20000	3.5619	4.1721	4.4739	5.0070	

molecular systems, obtained by the two procedures. In addition, a comparison is reported of viscosity-type collision integrals, not affected by excitation exchange, obtained by Sourd et al.,[9] showing a satisfactory agreement with $\sigma^2\Omega_c^{(2,2)*}$ values, both being derived within the traditional multipotential approach.

The percentage relative error is within 30% below 10 000 K for both atom−atom and atom−ion interactions, whereas the discrepancies increase with the temperature. The error estimation should, however, account for the low-accuracy characterizing of the short-range and long-range (dissociation limit), either for ab initio interaction curves or HH potentials modeled from spectroscopic data with respect to the region of intermediate distances. It results in a greater uncertainty of the classical collision integrals in the high- and low-temperature regions, affected by short and long-range interaction, respectively.

Moving to interactions involving higher excited colliding partners, relevant to higher dissociation limits and not presented here, significant deviations are found, even in the intermediate temperature region (40%), but the reliability of results derived in the classical approach is strongly compromised by the few available electronic terms actually included in the calculation with respect to the theoretically predicted number.

The ultimate validation of the phenomenological approach proceeds through the oxygen system (parameters of phenomenological potentials are reported in Table 4) by comparison with two series of data available in the literature,[8,11] based on a complete (62 valence states) multipotential traditional approach. The reevaluation of O_2 collision integrals in ref 11 is based on more accurate ab initio potentials for molecular electronic states with respect to the oldest set of results,[8] which suffered by the limited internuclear distance interval of used potential energy curves.

TABLE 4: Parameters of Phenomenological Potential for Interactions Relevant to Oxygen ($\alpha^{^3P} = 0.80$ Å^3,[29] $\alpha^{^1D} = 0.8039$ Å^3, $\alpha^{^1S} = 0.8371$ Å^3,[30]) Excited States

interaction		ε_0 (meV)	r_e (Å)	β	m
O(^{3}P)	O(^{3}P)	5.763	3.423	6.898	6
	O(^{1}D)	5.772	3.424	7.346	6
	O(^{1}S)	5.846	3.434	7.341	6
O(^{1}D)	O(^{1}D)	5.781	3.425	8.689	6
	O(^{1}S)	5.855	3.435	8.671	6
O(^{1}S)	O(^{1}S)	5.933	3.445	8.653	6

Since the viscosity-type collision integrals are not affected by resonant excitation exchange in asymmetric collisions, the observed deviations could give indication of the accuracy of the proposed procedure. A general satisfactory agreement is found between data sets in the considered temperature range (see Figure 1), and the percentage relative error is confined below 25% with respect to the results in ref 11. The error analysis should also take into account that the traditional multipotential procedure, including all electronic term contributions, is based in refs 8 and 11 on a rigid classification of repulsive (decaying exponential function) and bound (Morse function) states that could affect data accuracy.

Resonant Charge and Excitation Exchange Processes

The proposed phenomenological approach, as already pointed out, does not account for the contributions to odd-l collision integrals coming from inelastic channels, represented by the resonant charge-exchange and excitation-exchange processes occurring in atom−parent ion and asymmetric atom−atom interactions, respectively. The effective collision integral results from the following relation,[33]

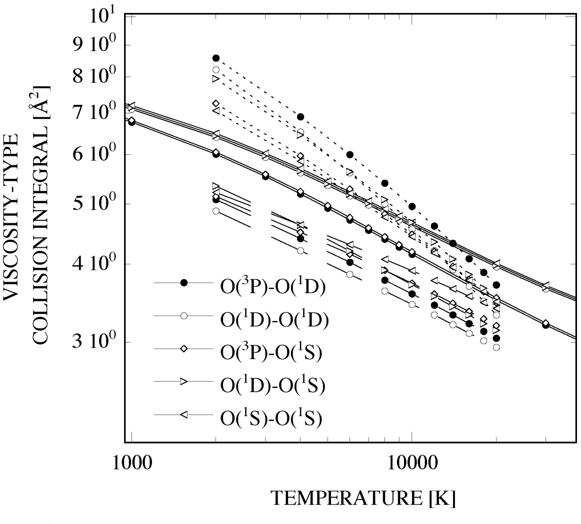

Figure 1. Viscosity-type collision integrals for O−O* interactions (continuous lines) from a phenomenological approach, as compared with results by Capitelli et al.[8] (dashed lines) and by Laricchiuta et al.[11] (dotted lines).

$$\Omega^{(l,s)*} = \sqrt{\left(\Omega_{\mathrm{el}}^{(l,s)*}\right)^2 + \left(\Omega_{\mathrm{in}}^{(l,s)*}\right)^2} \qquad l = \mathrm{odd} \qquad (4)$$

The inelastic term, $\Omega_{\mathrm{in}}^{(l,\,s)*}$, is estimated by means of a closed formula, suggested by Devoto,[34] for a linear dependence of the square root of charge transfer cross section on the collision velocity.

For the resonant charge exchange process, occurring in atom−parent ion collisions, reference is made to a recent paper[13] in which the corresponding cross sections have been derived using the asymptotic theory considering different momentum coupling schemes for those interactions between nitrogen atoms and ions allowed by single-electron transition. Concerning the exchange of excitation in asymmetric collisions between nitrogen atoms, few references can be found in the literature,[9,35] and in this work, it is reevaluated adopting an asymptotic approach and considering for these cases of dipole-forbidden electronic transitions the simultaneous transition of two electrons between the two ionic cores. The exchange interaction has an analytical expression,[36] depending on the quantum numbers characterizing the state of valence electrons undergoing the resonant process, and present results are obtained including only terms with null axial projection ($l = 1$, $m = 0$) representing the main contribution.[37] This approach predicts higher values than those obtained by the evaluation of gerade-ungerade splitting from potential energy curves;[9,35] however, the direct estimation could be affected by the lower accuracy characterizing the region of large internuclear distances, where the process takes place favorably.

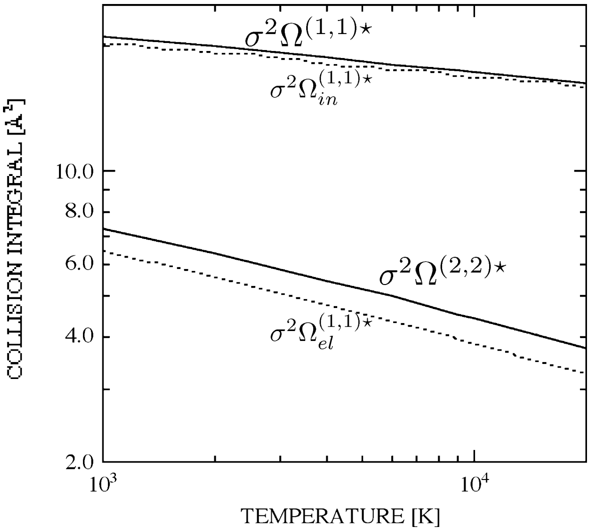

Figure 2. Effective diffusion-type collision integral with elastic and inelastic components and viscosity-type collision integral as a function of temperature for the asymmetric N(^{4}S)−N(^{2}D) interaction.

As generally observed, the inelastic contribution is significantly higher with respect to the elastic one, especially in the high temperature region, dominating the temperature-dependence of the effective diffusion-type collision integral in atom−atom and atom−ion interactions (see Figures 2 and 3).

The charge exchange also dominates the dependence of $\sigma^2\Omega^{(1,1)*}$ on the electronic excitation of colliding partners, determined by the corresponding cross sections, as shown by the analysis at fixed temperature of two series of interactions: (1) ground state nitrogen ion and progressively excited atomic partner (Figure 3a) and (2) excited nitrogen atom and progressively excited ionic partner (Figure 3b).

Differently, the quantum-state dependence of the pure elastic diffusion-type collision integral is ruled by the features of the phenomenological interaction potential.

Interactions Involving High-Lying Excited States

In the frame of phenomenological approach and for the case of interactions involving high-lying excited states, the analytical function adopted for the average interparticle potential should be modified with respect to the previous potential (3) to properly describe the nature of interaction forces between two highly excited species.

The eligible system for the model validation is the H(n)−H(n) interaction. In fact, a lot of work has been done for the theoretical study of the so-called Q(2) states, that is, doubly excited states of H_2 molecule, dissociating into two H(n = 2) excited atoms.[38−40] The coupling scheme of electronic and spin angular momenta in the interaction of two 2s or 2p hydrogen atoms results in 22 electronic molecular terms $(4)^1\Sigma_g^+$, $(4)^3\Sigma_u^+$, $^1\Sigma_u^+$, $^1\Sigma_u^-$, $^3\Sigma_g^+$, $^3\Sigma_g^-$, $(2)^{1,3}\Pi_{g,u}$, $^1\Delta_g$, and $^3\Delta_u$. Previous ab intio data suffered from the limits of energy calculation in the short and long-range regions dominated by overlap/exchange and by weak van der Waals forces, respectively.

Recently, the potential energy curves for these excited states were derived with high accuracy using a new molecular

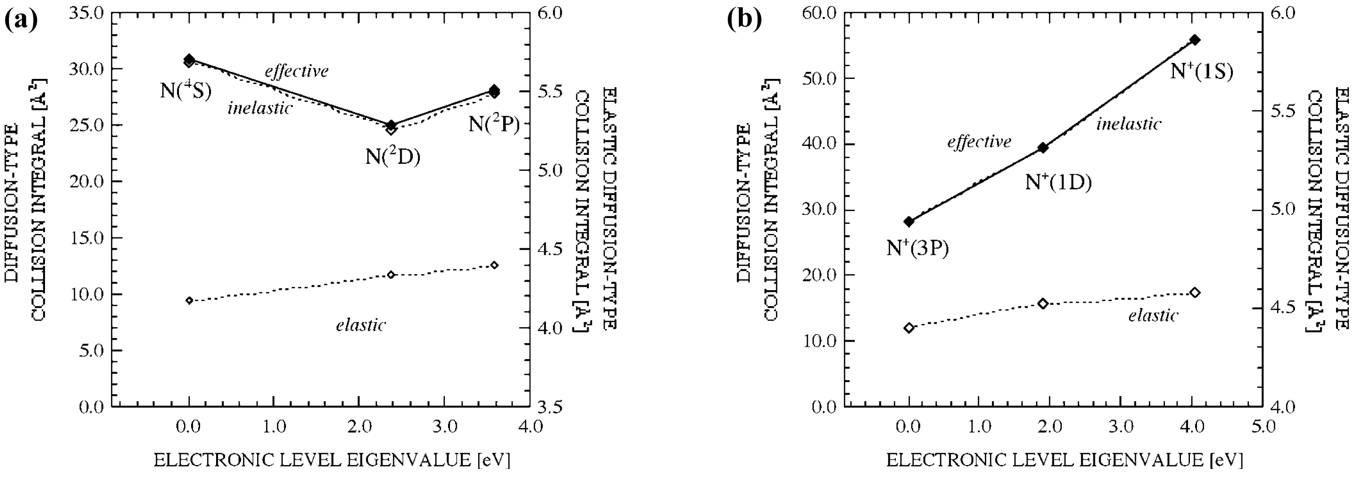

Figure 3. (a) Effective diffusion-type collision integral, with elastic and inelastic components, as a function of quantum state of the atomic collision partner in N^+ (^{3}P)−N * interactions, at $T = 10^4$ K. (b) Effective diffusion-type collision integral, with elastic and inelastic components, as a function of the quantum state of the ionic collision partner in $(N^+)^*$−N*(^{2}P) interactions, at $T = 10^4$ K.

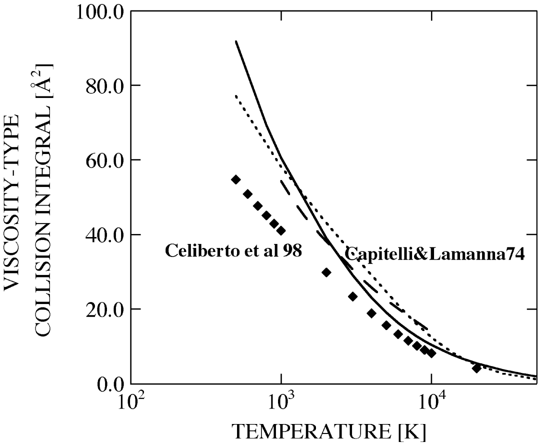

Figure 4. Viscosity-type collision integrals for H(n = 2)−H(n = 2) interaction as a function of temperature as compared with results in the literature: (—) present multipotential approach, (− − −) multipotential approach by Capitelliand Lamanna[15] and by Celiberto et al.[16] (◆). Results of the phenomenological approach are also reported (• • •).

ab initio code based on B-splines and allowing the exploration of a wide range of internuclear distances (3.0−100.0 a_0) connecting the two extreme regimes without an interpolation procedure.[41]

In the present investigation, diffusion and viscosity-type collision integrals, averaged on different states with a statistical weight equal to state degeneracy, have been obtained by classical integration of those interaction potentials. Numerical results by Vanne et al.[41] have been cubic-spline-interpolated to accurately describe the potential features (small, long-range barriers; double minima; short-range minima), whereas the repulsive interaction has been described as

$$\ln[\varphi(r)] = \alpha_{\rm rep} - \beta_{\rm rep} r \qquad (5)$$

obtaining parameters $\{\alpha_{\rm rep}, \beta_{\rm rep}\}$ by interpolation of the first two points.

Results have been proposed in the past by different authors, following the same multipotential approach, but on the basis of a different choice of potential energy curves for the electronic states involved. In the paper by Capitelli and Lamanna,[15] reference was made to the pioneering work of Linder[38] describing accurately the manifold of states correlating with H(2)−H(2) in the medium- and long-range regions. Celiberto et al.[16] performed calculations of quantum transport cross sections with an appropriate statistic for identical particles, and the interaction potentials were obtained in an ab initio full-CI step for selected symmetries. In fact, in this case, collision integrals were calculated averaging only contributions from two electronic states $^1\Sigma_g^+$ and $^1\Pi_g$, whose potential compare well with those in literature.[39]

In Figure 4, the temperature dependence of viscosity-type collision integral is displayed and compared with results of literature. As is well-known, the high-temperature behavior is dominated by the short-range repulsive interaction forces, whereas the long-range interaction modulates the low-temperature profile. Inspection of Figure 4 indicates that the present accurate results agree with older ones in different temperature regions. This evidence can be rationalized considering that Linder potentials[38] are accurate in the dissociation limit, but a lack of information for atoms closely approaching compromised the estimation of Capitelli and Lamanna in the high-temperature region. In contrast, the results of ref,[16] well-reproducing the repulsive interaction, are affected by the poor information in the weak-interaction region, underestimating the corresponding low-temperature value of the collision integral.

In the phenomenological approach, the average interaction between excited hydrogen atoms has been described by using a potential function that results from the combination of the long-range attractive part in eq 3 (between highly polarizable species, exhibiting an high tendency to deformation) and a short-range coulomb potential, due to core−core-repulsion.

$$\varphi = g\left[\frac{\mathrm{e}^2 q^2}{r(4\pi\mu_0)}\right] + (1 - g)\left[-\varepsilon_0 \frac{n(x)}{n(x) - m}\left(\frac{1}{x}\right)^m\right] \qquad (6)$$

The function g is the switching function smoothly joining the two curves, expressed as

$$g = \frac{1}{1 + \left(\frac{r}{r_0}\right)^2 \exp\left[\frac{(1/r_0 - 1/r)}{\delta}\right]} \qquad (7)$$

and characterized through the inflection point $r_0 = 1.25\ r_{\rm e}$ and the amplitude $\delta = 0.05$.

In the case of H(2)−H(2), the potential parameters $\{r_e, \varepsilon_0, \beta\}$ of the attractive component have been determined using the phenomenological relations already assumed for the interaction between ground-state particles,[17] but instead of neutral particles, the interaction is modeled considering the encounter of a neutral excited atom of polarizability $\alpha_{\rm pol} = 24$ Å^3 with an ion of *effective* charge $q = 0.5$ ($m = 4$). From a physical point of view, it corresponds to considering that, as the two excited species approach each other, one of the two diffuse electron density distributions is displaced backward, leaving the nuclear charged partly unshielded and mimicking an ion-neutral attraction, inducing the deformation of the electronic distribution of the other partner. (In the case of symmetric collisions, when partners are identical, the choice of modeling the interaction in this asymmetric way is less intuitive than in the more general case of collision between different chemical species. However, it is reasonable that polarization effects, dominant at long range, can be instantaneously represented, taking into account the simple deformation of each electronic cloud without any constraint due to the symmetry.) As the interparticle distance decreases, the penetration into the electronic clouds becomes more effective, generating a repulsion better described by a Coulomb interaction of two charged particles. It is relevant to stress that the proposed phenomenological potential simulates the behavior of the full interaction. The predictions are expected to be reliable, especially when the colliding system probes mostly the average interaction at intermediate and large interatomic distances and details of the anysotropy, such as those due to gerade−ungerade symmetry effects (emerging as the distance descreases), play a minor role.

The $\sigma^2\Omega^{(2,2)*}$ collision integral obtained by the proposed phenomenological approach is also reported in Figure 4, finding a satisfactory agreement.

The paper by Celiberto et al.[16] has the great merit of investigating the collision integral dependence on the principal quantum number in symmetric collisions H(n)−H(n) up to n =

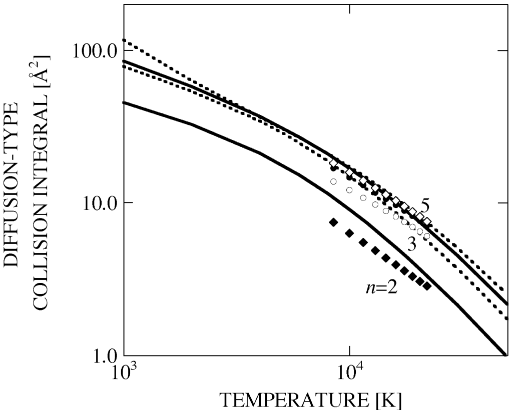

Figure 5. Diffusion-type collision integrals for H(n)−H(n) interaction as a function of the temperature, obtained with the phenomenological approach (continuous line, n even; dotted line, n odd) compared with the results in ref 16 (markers).

5. Of course, on increasing the n value, the interaction results from contributions of an increasing number of possible collisional pairs (e.g., H($n = 3$)−H($n = 3$) ≡ H(3s, 3p, 3d)−H(3s, 3p, 3d)) and, in turn, an increasing number of electronic molecular terms dissociating in that limit. Authors have chosen the one-state representation for each limit, selecting the lowest root of the $^1\Sigma_g^+$. Transport cross sections are found to scale with the $n = 2$ value as the inverse of the screened constant in Coulomb interaction.

In the phenomenological potential eq 6 the charge, q, is assumed to depend on the principal quantum number, n,

$$q(n) = 1 - \frac{1}{\sqrt{2n}} \tag{8}$$

In considering highly excited states, the polarizability value has been estimated as an average value over quantum sublevels by using the formula proposed by Hey[42] while the effective charge increases up to the limit of H^+−H^+ interaction; that is, $q = 1$. In Figure 5, the diffusion-type collision integrals obtained in the frame of the phenomenological approach are reported for $2 \le n \le 5$ and compared with results by Celiberto et al.[16]

As can be appreciated, the method satisfactorily reproduces the increase in the Ω value due to the electronic excitation of the collision partners. Actually, the agreement is better at higher temperatures in a coulomb repulsive regime with percentage relative errors below 10% for $n > 2$ for $T > 13\,000$, whereas in the low-temperature region discrepancies up to 25% are found. The $n = 2$ case is characterized by higher deviations ranging from 30 to 17% in the considered temperature interval.

Conclusions

The estimation of the role of excited species in affecting the transport properties of gas mixtures goes through the evaluation of corresponding collision integrals and their dependence on the quantum state of the collision partners. Both quantum and classical approaches based on averaging procedures require the accurate knowledge of potential energy curves for all the molecular electronic terms characterizing the interaction. However, the theoretical investigation of the electronic structure of highly excited electronic states is also a computationally demanding task. In this framework, the use of approximate theories or model potentials reproducing the main features of the average interaction could be a valuable tool. The phenomenological approach, developed for the interpretation of crossed beam experiments and then successfully used in the evaluation of elastic transport cross sections for ground-state interactions of unknown systems, could be a good candidate. It should be stressed that the proposed method does not account for the inelastic contribution coming from the resonant charge or excitation transfer occurring in atom−atom and atom−parent ion interactions, respectively. Actually, the inelastic term, affecting the odd-order collision integrals, has been shown to be the dominant contribution and also to have a strong dependence on the principal quantum number. The evaluation of this contribution could be performed in the framework of the asymptotic theory,[37,43,44] obtaining reliable results.

In this paper, the phenomenological approach has been validated for the estimation of different moments of elastic cross sections for interactions involving low-lying excited states in nitrogen and oxygen systems, also deriving results in the classical approach and showing reasonable agreement. The possibility of extending the method to high-lying excited state interactions is explored, considering hydrogen system as a benchmark. The results are very promising, although the model needs to be improved and tested with different systems to accommodate all possible physical situations.

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