Autoionization Processes Involving Molecules of Atmospheric Interest: A Computational Test for Ne^*-N_2 System

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Abstract. This paper provides basic aspects of the stereodynamics of autoionization reactions, triggered by collisions of N_2 molecules with metastable neon atoms, $Ne^*(^3P_{2,0})$, that are of great relevance for the balance of phenomena occurring in atmospheric environments under various conditions. A computational analysis based on the long-range intermolecular forces involved, some of chemical and other of physical origin, allows a first attempt in order to reproduce experimental data from our and other laboratories. This is a good test of the reliability of our recently proposed semiclassical model for atom-atom self-ionization processes and here extended to a simple atom-molecule system.

Keywords: Autoionization · Stereo-dynamics · State to state · Charge transfer · Transition state · Electron spectroscopy · Astrochemistry

1 Introduction

It is well known that the stable-closed shell nature of noble gas atoms Ng (Ng = He, Ne, Ar, Kr and Xe) explains their chemical inertness [1]. On the other hand, when Ng is excited in electronic metastable states (producing Ng^* atom) it assumes an open shell structure and because of its high energy content becomes extremely reactive. In general, Ng^* atoms live for a time sufficient long to give several collisions with other partners even under gaseous rarefied conditions of pressure [2–6]. Ng^*can be formed by collisions of Ng atoms with cosmic rays and/or energetic electrons and their two body collisions with neutral atomic/molecular M partners can promote autoionization reactions, from sub-thermal (cold chemistry) [7], of relevance in astrochemistry [8, 9], up to hyper-thermal (hot chemistry) conditions, of importance in combustion and flames [10, 11], with the formation of NgM^+ (associate ion) and/or Ng + M^+(Penning ion) + electrons as products. Highest energetic He^* and Ne^* atoms trigger autoionization with

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most part of neutral species and in the case of molecular partners also ions coming from the fragmentation of parent M^+ can be formed [2–4].

Because of their relevance in the balance of microscopic processes occurring in plasmas, electric discharges and laser systems, autoionization reactions have been investigated in bulk, and under single collision conditions with the molecular beam technique [2–6]. Important experimental findings have been provided by measuring the collision energy dependence of total and partial (i.e., referred to specific reaction channels) ionization cross sections and of Penning ionization electron spectra (PIES). All these findings depend on different features of the optical potential, formerly introduced for the description of nuclear reactive collisions [12], whose real part drives the collision dynamics while its imaginary part, triggering the passage from neutral reagents to ionic products, accounts for the "opacity" of the system [3, 4]. However, up to day information on important details of the intermolecular forces controlling the optical potential, as their nature and their dependence on the relative orientation of involved partners, and consequently on their effect on the reaction stereo-dynamics, is rather limited.

Recently, we have proposed an applied a new/original method for the detailed representation of autoionization processes promoted by collisions of $Ne^*(^3P_{2,0})$ with Ar, Kr and Xe and such study provided an internal consistent rationalization of available experimental findings [13–15]. In particular, the proper characterization of the intermolecular forces that drive the atom-atom reaction dynamics casted light on basic/innovative aspects concerning rearrangement and angular momentum coupling of valence electron. Obtained results must be considered of general interest for the control of many other elementary chemical reactions. In particular, the application of our method suggests that autoionization can occur through the competition of two alternative (*direct/indirect*) reaction mechanisms driven by the selectivity of intermolecular forces of different nature [14, 15]. The *direct mechanism*, dominant at short separation distances of reagents, is basically controlled by chemical forces due to charge (electron) transfer (CT) effects. The *indirect mechanism*, prevalent at large separation distances, originates from weaker forces of more physical origin, as those due to dispersion, induction-polarization contributions and those promoting spin-orbit and centrifugal-Coriolis effects. Moreover, while the *direct mechanism* controls the evolution of prototype elementary *oxidation reaction*s [14, 15], the *indirect mechanism* triggers typical *radiative* (*photo*)-*ionization processes* [16, 17].

The present target is to extend this method to study autoionization reactions of molecules and a preliminary objective to be achieved is the correct identification of nature and strength of intermolecular forces controlling structure and stability of the reaction transition state (TS). It is of relevance to note that intermolecular forces involved in autoionization reactions involving molecules are usually stronger, more anisotropic and including additional components respected to the atom-atom case [13, 14].

2 Modelling the Internuclear Interaction

The computational model used to describe both atom-atom and atom-molecules autoionization reactions is based on the Optical Potential Model (OPM) proposed by Hans Bethe in 1940 [12], where a complex potential W is used to describe the microscopic

autoionization dynamics according to the following equation:

$$W = V - \frac{i}{2}\Gamma \tag{1}$$

V is the real part describing the $Ng^* + M$ interaction in the incoming collision (where M can be an atomic or molecular target) and Γ is the imaginary part that takes into account the probability of the autoionization of the intermediate collisional complex $[Ng\text{---}M]^*$, which is the transition state (TS) of the reaction [16, 18, 19].

The novelty of our semiclassical treatment, already proposed and successfully applied to simple atom-atom autoionization processes [13–15, 20, 21] consider the two V and Γ components as interdependent [6, 14, 15]. The general treatment can be found in details in refs. [14, 22] pointing out the differences with previous adopted models for autoionization processes [23, 24]. Its application and obtained results in the description of state-to-state $Ne^*(^3P_{2,0})$-Ar, Kr and Xe atom-atom autoionizing systems are reported in refs. [13–15]. The selectivity of the electronic rearrangements triggering the two microscopic mechanisms operative in such atom-atom auotionization reactions (see the *direct* and *indirect mechanisms* mentioned above) has been related to the angular momentum couplings by Hund's cases and is fully described in ref. [23]. Here, in the following subsection, a first computational attempt to extend our treatment to the atom-molecule case is done, considering the simple Ne^*-N_2 system which is relevant for an atmospheric point of view. Further details concerning the computational procedure and the modelling of the intermolecular potential are given in refs. [25, 26].

2.1 Extension to Autoionization Reactions Involving Molecules

Preliminary, it is convenient to consider N_2 and N_2^+ as isotropic partners. According to the general features discussed in details in refs. [14, 22], also for atom-molecule autoionizing systems is important to evaluate only C_x (C_x and C_y are the radial dependence of the Σ character coefficients in entrance, $[Ng\text{---}M]^*$, and in exit, $[Ng\text{---}M]^+$, channels, respectively [14]): $C_y = 1$ is assumed to hold at all internuclear distances, R, as suggested by the electronic structure of the N_2^+ product, extending the previous relations obtained in the case of atom-atom autoionization:

$$V_{|2,0>}, V_{|2,1>} = cos^2\alpha V_\Sigma + sin^2\alpha V_\Pi \tag{2}$$

$$V_{|0,0>} = sin^2\alpha V_\Sigma + cos^2\alpha V_\Pi \tag{3}$$

$$V_{|2,2>} = V_\Pi \tag{4}$$

$$cos^2\alpha = \frac{1}{2} + \frac{\left(1 - \frac{9V_2}{5\Delta}\right)}{4\sqrt{2}\sqrt{1 + \left[\left(\frac{1 - \frac{9V_2}{5\Delta}}{2\sqrt{2}}\right)\right]^2}} \tag{5}$$

Where, for all channels: the effective adiabatic potential energy curves are expressed as $V_{|J;\Omega>}$ (J is the total electronic angular momentum quantum number, defining also

the spin orbit level, while Ω quantizes the absolute projection of the **J** along *R*); the coupling terms $A_{\Lambda-\Lambda'}$ between entrance and exit channels (i.e. $A_{\Sigma-\Sigma}$, $A_{\Pi-\Pi}$, $A_{\Sigma-\Pi}$ and $A_{\Pi-\Sigma}$), on the basis of Σ and Π molecular character of initial and final states of the system involved in the electron exchange have been adopted (Σ ($\Lambda = 0$) and Π ($\Lambda = 1$) are the molecular states of different symmetry and accessible to the colliding system – see ref. [14] for more details); for both entrance and exit channels, V_2, that we have identified with the anisotropic configuration interaction between entrance and exit channels differing for one electron exchange (see refs. [14, 15]), has been represented by an exponential decreasing function, defined by a pre-exponential factor A and an exponent α which is given by Eq. (5); Δ is the energy splitting SO between fine atomic sublevels, identified by the quantum number J.

For such reactions it can be assumed that only $A_{\Sigma-\Sigma}$ and $A_{\Pi-\Sigma}$ couplings are effective for the electron rearrangements, since they are also the most important couplings in atom-molecule processes of present interest. Here, it is convenient to identify $A_{\Sigma-\Sigma}$ and $A_{\Pi-\Sigma}$ with A_{DM} and A_{IM}. They represent, respectively, the coupling that promotes the *direct mechanism* (*DM*), through the control the chemical reactivity, and the *indirect mechanism* (*IM*) to which important contributions come from polarization, that stimulates photo-ionization, spin-orbit and Coriolis couplings *effects.*

Accordingly, the following relations are obtained for state-to-state *Γ* components:

$$\Gamma_{|0,0\rightarrow ions>} = A_{DM}\, C_x + +A_{IM}\,(1 - C_x) \tag{6}$$

$$\Gamma_{|2,0\rightarrow ions>} = A_{DM}\,(1 - C_x) + A_{IM}\, C_x \tag{7}$$

$$\Gamma_{|2,1\rightarrow ions>} = A_{DM}\,\frac{3}{4}(1 - C_x) + A_{IM}\left(\frac{3}{4}C_x + \frac{1}{4}\right) \tag{8}$$

$$\Gamma_{|2,2\rightarrow ions>} = A_{IM} \tag{9}$$

On this ground, it is possible to obtain the *Γ* dependence only on **J** of the entrance channels and averaged on Ω:

$$\Gamma_{|0\rightarrow ions>} = A_{DM}\, C_x + +A_{IM}\,(1 - C_x) \tag{10}$$

$$\Gamma_{|2\rightarrow ions>} = \frac{1}{2}[A_{DM}\,(1 - C_x) + A_{IM}\,(1 + C_x)] \tag{11}$$

The *Γ* averaged on the spin orbit states of reagents is given by:

$$\Gamma_{|ions>} = w_0[A_{DM}\, C_x + A_{IM}\,(1 - C_x)\Big] + \frac{w_2}{2}[A_{DM}\,(1 - C_x) + A_{IM}\,(1 + C_x)\Big] \tag{12}$$

If it is assumed that $\frac{w_0}{w_2} = \frac{1}{3}$ (the statistical weight ratio in the case of ^3P_J open shell atomic species like $Ne^*(^3P_{2,0})$, see ref. [14]), the final relation is obtained

$$\Gamma_{|ions>} = \frac{1}{8}[A_{DM}\,(3 - C_x) + A_{IM}\,(5 + C_x)] \tag{13}$$

Now, if we can assume that only $A_{\Pi-\Pi}$ and $A_{\Sigma-\Pi}$ are effective for the reaction we obtain the same equation with inverted coefficients is otained. Specifically:

$$\Gamma_{|0,0\rightarrow ions>} = A_{IM}\, C_x + +A_{DM}\,(1 - C_x) \tag{14}$$

$$\Gamma_{|2,0\rightarrow ions>} = A_{IM}\,(1 - C_x) + A_{DM}\, C_x \tag{15}$$

$$\Gamma_{|2,1\rightarrow ions>} = A_{IM}\,\frac{3}{4}(1 - C_x) + A_{DM}\left(\frac{3}{4}C_x + \frac{1}{4}\right) \tag{16}$$

$$\Gamma_{|2,2\rightarrow ions>} = A_{DM} \tag{17}$$

Accordingly, also previous equations modify consistently. For instance:

$$\Gamma_{|ions>} = w_0[A_{DM}\,(1 - C_x) + A_{IM}\, C_x\Big] + \frac{w_2}{2}[A_{DM}\,(1 + C_x) + A_{IM}\,(1 - C_x)\Big] \tag{18}$$

2.2 Modelling the Intermolecular Interaction on Ne^*-N_2 Autoionizing System

A proper study of autoionization processes involving molecules must include also the dependence on the molecular orientation. For all the components of the interaction (see the real part V of the OPM of Eq. (1)) an expansion in Legendre polynomials is adopted, where $P_0 = 1$ and θ defines the orientation of the molecules respect the Ne^* atom ($\theta = 0$ indicates a collinear approach):

$$P_2(\cos\theta) = \frac{3cos^2(\theta) - 1}{2} \tag{19}$$

This procedure concerns both the real and the imaginary part of the optical potential.

2.2.1 The $[Ne\text{---}N_2]^*$ Entrance Channel

For atom-atom systems a manifold of potential energy curves, properly coupled and depending on R, describes the dynamical evolution of the processes. For atom-molecule systems the dynamics is controlled by a manifold of potential energy surfaces, whose main features are here obtained extending the atom-atom treatment.

In the formulas of the intermolecular potentials $V_{|J,\Omega>}$ introduced for atom-atom systems [14], the term $V_0(R)$ ($V_0 = \frac{1}{3}(V_\Sigma + 2V_\Pi)$, describing the spherical average interaction component, is now replaced by:

$$V_0(R,\theta) = V_{nel}^{i-n}(R,\theta) + V_{elect}(R,\theta) \;\text{ when }\; R < R_0 \tag{20}$$

$$V_0(R,\theta) = V_{nel}^{n-n}(R,\theta) \;\text{ when }\; R > R_0 \tag{21}$$

where $V_{nel}^{i-n}(R,\theta)$ and $V_{nel}^{n-n}(R,\theta)$ are the components of the potential representing for ion-neutral and neutral-neutral interactions, respectively. For them it is used an

Improved Lennard Jones (ILJ) [25–28] function having the $\varepsilon(meV)$ and $R_m(\text{Å})$ parameters defined as it follows in terms of the polarizability of the neutral and ionic species involved:

$$-n-n \text{ case } R_m(\theta) = 5.70 + 0.00\ P_2(\cos\theta);\ \varepsilon(\theta) = 3.15 + 0.00\ P_2(\cos\theta) \quad (22)$$

$$-i-n \text{ case } R_m(\theta) = 2.96 + 0.35\ P_2(\cos\theta);\ \varepsilon(\theta) = 114.0 + 16.0\ P_2(\cos\theta) \quad (23)$$

The further contribution $V_{elect}\ (R, \theta)$ here added describes the electrostatic interaction between the ion Ne^+, nascent as a consequence of the *3s* electron polarization of Ne^* in the collision complex, and the electric permanent quadrupole of N_2. For the term $V_{elect}(R, \theta)$, given in meV, the formulation adopted in the case of the Ar^+-N_2 interaction [29] has properly extended, leading to:

$$V_{elect}(R, \theta) = -\frac{3996}{R^3} P_2(\cos\theta) \quad (24)$$

As previously done for the atom-atom case [14], the two types of interactions must be combined with a Fermi function dependent on R_0 and d. Also here, $R_0 = 3.72$ Å is the distance where the two combined limiting potential forms have the same weight, while $d = 0.5$ Å describes how fast the transition occurs.

In the adiabatic formulation of $V_{|J,\Omega>}$ appears also the V_2 term, $V_2 = \frac{5}{3}(V_\Sigma - V_\Pi)$, due to the electronic anisotropy of the P atom and related to the charge transfer (CT) term [14]. In the atom-atom case has been used a simple $V_2(R)$, while now for the atom-molecule systems a function $V_2(R, \theta)$ must be adopted. For the Ne^*-N_2 system with the formation of the N_2^+ ion in its ground electronic state ($^2\Sigma$) the following parameterization, estimated on the basis of the noble gas systems already investigated and the couplings identified for the prototype $(Ar\text{-}N_2)^+$ system [29], can be used:

$$V_2(R, \theta) = (1.4 \cdot 10^7 + 4.0 \cdot 10^6 \cdot P_2(\cos\theta)) \cdot e^{-4.32 \cdot R} \quad (25)$$

2.2.2 The $[Ne—N_2]^+$ Exit Channel

In this case, the representation of the real part V of the OPM (see Eq. (1)) is easier than before being facilitated by the fact that there is no spin-orbit coupling that mixes the states with different electronic symmetry. Therefore, in the case of N_2^+ formation in its ground electronic state $^2\Sigma$, we can use directly the following expression:

$$V_t(R, \theta) = V_{nel}^{i-n}(R, \theta) + V_{CT}(R, \theta) \quad (26)$$

Note that the Eq. (26) also includes the coupling for CT with the excited electronic state $^2\Pi$ of N_2^+ which, even if it cannot be formed by autoionization since Ne^* does not have enough energy, is part of the configuration interaction [14, 15].

For the $V_{nel}^{i-n}(R, \theta)$ term the following parameters can be used:

$$R_m(\theta) = 3.30 + 0.35\ P_2(\cos\theta);\ \varepsilon(\theta) = 30.0 - 13.2\ P_2(\cos\theta) \quad (27)$$

While the $V_{CT}(R,\theta)$ term becomes equal to $\simeq -\frac{2}{5}\ V_2(R,\theta)$.

In the case of the formation of N_2^+ in the $^2\Pi$ excited electronic state, the formulation of $V_{nel}^{i-n}(R,\theta)$ term remains the same than before, while the $V_{CT}(R,\theta)$ term becomes equal to $\simeq\ -\frac{3}{5}\ V_2(R,\theta)$, as suggested by the greater overlap and greater proximity between the entrance and exit ionic state, as demonstrated previously for the prototype system $(Ar\text{-}N_2)^+$ [29].

2.2.3 Definition of Γ(R,θ) and Autoionization Probability

The $V_2(R,\theta)$ term, defined in Eq. (25), it is also used to calculate the coefficient C_x which appears in the weight of the *direct* and *indirect* mechanisms, i.e. in the weight with which to combine the A_{DM} e A_{IM} couplings terms necessary to determine the imaginary part Γ of the OPM in its various components according to Eqs. (6)–(18). The definition of the couplings terms can be done as it follows:

$$A_{DM}\,(meV) = (5.0 \cdot 10^6 + 5.0 \cdot 10^5 \cdot P_2(\cos\theta)) \cdot e^{-4.32 \cdot R} \tag{28}$$

$$A_{IM}\,(meV) = (1.9 \cdot 10^3 + 3.8 \cdot 10^2 \cdot P_2(\cos\theta)) \cdot e^{-2.20 \cdot R} \tag{29}$$

The full representation of Γ allows for the evaluation of the probability of self-ionization for the system under consideration based on the general treatment extensively described elsewhere [24, 26]. Indeed, along the element dR, at the distance R, during a collision with asymptotic speed g and a collision energy E, with impact parameter b, the probability that the system ionizes is given by Eq. (30) below

$$P(R)dR = \frac{\Gamma(\mathrm{R})}{\hbar g\left[1 - \frac{V(R)}{E} - \frac{b^2}{R^2}\right]^{\frac{1}{2}}} dR. \tag{30}$$

3 Experimental Determination of the Cross Sections

In our laboratory we are able to measure either total and partial ionization cross sections discriminating all the possible product ions by mass spectrometry in a crossed beam apparatus, which has been presented in detail in previous papers [30–33]. Shortly, such apparatus consists of two beams, one of metastable rare gas atoms, generated by electron bombardment (two possible effusive and supersonic beam sources are available with the possibility to change the nozzle temperature and to use the seeded beams technique as described in refs. [34–36]), and the other one of the target molecules in the ground state, that cross at 90°. The product ions are extracted from the scattering volume by an electric field (usually ≈150 V/cm).

For the total ion intensity measurement, the ions are directly detected by a channel electron multiplier. For the mass analysis the product ions are focused, mass analyzed by a quadrupole filter, and detected by another channel electron multiplier.

A time-of-flight device was used to obtain the velocity (or collision energy) dependence of cross sections, including those of interest for the present study. A scheme of our crossed molecular beam device is reported in Fig. 1.

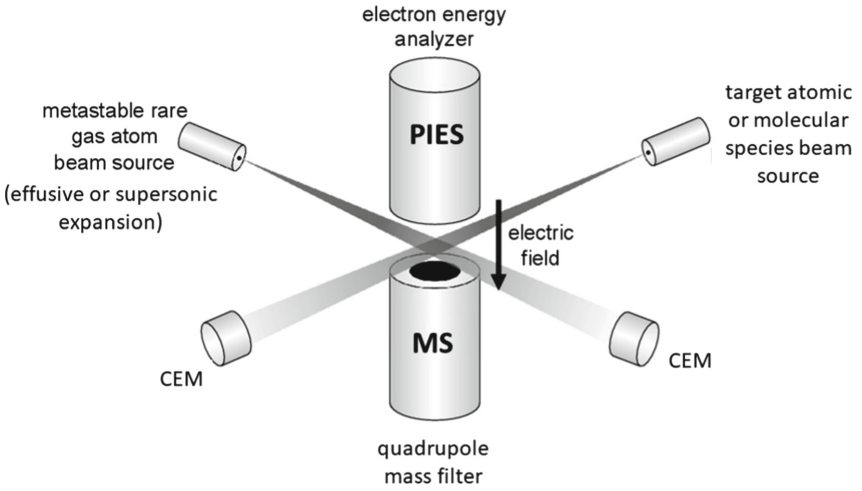

Fig. 1. The crossed molecular beam apparatus working in the Perugia laboratory coupled with mass spectrometry (MS) and Penning ionization electron spectroscopy (PIES). To monitor the metastable rare gas atom beam and the target atomic or molecular species beam, two channel electron multipliers (CEM) are used.

4 Computational Results and Comparison with Experimental Cross Sections

A first attempt has been done in the calculation of the manifold of potential energy surfaces for the $Ne^*(^3P_{2,0})$-N_2 used as a test system applying the computational procedure described in Sect. 2. Involved interaction potentials have been used to calculate the cross sections for the two open channels in the experimentally investigated collision energy range (30–120 meV in our laboratory [37] and 8–60 meV by the Osterwalder group [38]) that are reported below:

$$Ne^*\left(^3P_{2,0}\right) + N_2 \rightarrow Ne + N_2^+ + e^- \text{ (Penning ionization)} \tag{31}$$

$$\rightarrow NeN_2^+ + e^- \text{ (associative ionization)} \tag{32}$$

The results obtained are shown in Fig. 2 where a direct comparison between experimental and computational data can be done.

From Fig. 2 is evident that the experimental data obtained in the Perugia laboratory [37] indicate that in our case the production of the associative ionization (see Eq. (32)) is very low. This is a clear indication that in our experiment performed at thermal collision energy (30–120 meV) there is a prevalent dissociation of the NeN_2^+ ion produced by the autoionization reaction between Ne^* and N_2. On the other hand, the data from the Losanna laboratory obtained in the sub-thermal regime of the collision energy (8–60 meV) [38] are much higher than both our previous experimental determinations and the computational calculations performed according to the procedure illustrated in Sect. 2. This could be an evidence that for this system a clear orientational effect emerges

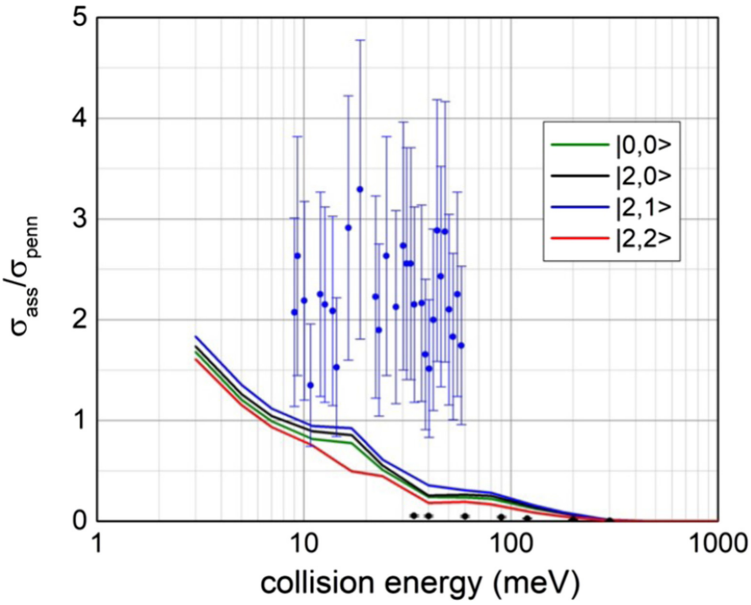

Fig. 2. The ratio between associative and Penning ionization cross sections (see Eqs. (31) and (32)) as a function of the collision energy for the $Ne^*(^3P_{2,0})$-N_2. The curves are the result of the computational calculation based on our model at a state-to-state level for the various $|J,\Omega\rangle$ states (see text). The points are the experimental data obtained in the Losanna laboratory (blue color) [38] and in the Perugia laboratory (black color) [37]. (Color figure online)

when low collision energies are probed. To clarify these effects, further investigations will have to be made, extending this first test on the Ne^*-N_2 system by investigating different angles of approach between the reagents. To this end, further studies are in progress in our laboratory.

5 Conclusions

The present paper extends a new semiclassical method recently proposed by our research group and succesfully applied to autoionization reactions involving Ne^* metastable atoms and simple atomic targets as Ar, Kr and Xe [14, 15] to the stereodynamical study of autoionization reactions of molecules in a quantum state-to-state condition. As a preliminary test has been investigated the $Ne^*(^3P_{2,0})$-N_2 system and useful comparison between experimental data and computational calculations of the Penning and associative ionization is reported showing that a clear orientational effect emerges when low collision energies are probed in the sub-thermal regime. Obtained results are encouraging and open the possibility to apply the proposed computational methodology to the autoionization reactions involving more complex molecules which are of great interest in several fields, including the balance of phenomena occurring in interstellar environments [39–41] and planetary atmospheres [42–44].

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