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New Insights on the Stereodynamics of Elementary Processes Controlled by Anisotropic Intermolecular Forces

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Abstract – Changes in atomic-molecular alignment and/or in molecular orientation, can affect strongly the fate of basic collision events. However, a deep knowledge of these phenomena is still today not fully understood, althoughit is of general relevance for the control of the stereodynamics of elementary chemical-physical processes, occurring under a variety of conditions, both in gas phase and at surface. In particular, understanding the mode-specificity in reaction dynamics of open-shell atoms, free radicals, molecules, atomic and molecular ions, under hyper-thermal, thermal and sub-thermal conditions is of fundamental importance for catalysis, plasmas, photo-dynamics as well as interstellar and low-temperature chemistry. In this paper new results on the role of atomic alignment effects on the stereodynamics of autoionization reactions will be presented and discussed.

Keywords: reaction stereodynamics; charge transfer; atomic alignment; autoionization processes

Riassunto – La variazione del tipo e grado di allineamento atomico-molecolare e/o di orientazione molecolare, può influenzare fortemente decorso e risultato finale di eventi collisionali. Tuttavia, una profonda conoscenza di questi fenomeni non è ancora oggi pienamente compresa, anche se è di rilevanza generale per il controllo della stereodinamica dei processi chimico-fisici elementari, che si verificano in una varietà di condizioni, sia in fase gassosa che su superficie. In particolare, comprendere la stereo-specificità delle dinamiche di reazione di atomi a guscio aperto, radicali liberi, molecole, ioni atomici e molecolari, in condizioni ipertermiche, termiche e sub-termiche è di fondamentale importanza per la catalisi, per la chimica dei plasmi, per la fotodinamica così come per la chimica interstellare e a bassa temperatura. In questo documento verranno presentati e discussi nuovi risultati sul ruolo degli effetti di allineamento atomico sulla stereodinamica delle reazioni di autoionizzazione.

Parole chiave: stereodinamica di reazione; trasferimento di carica; allineamento atomico; processi di autoionizzazione

Introduction

The knowledge of strength, anisotropy and radial dependence of the leading intermolecular interaction components is a crucial objective to assess the selectivity of the molecular dynamics under a variety of conditions. The charge transfer (CT), a basic component of the intermolecular interaction, whose role is often not fully understood, affects myriad of phenomena, including also the formation of intermolecular halogen and hydrogen bonds.

The focus of this paper is exclusively on the selective role of anisotropic CT on the stereodynamics of autoionization processes, also known as Penning or chemiionization phenomena (Siska 1993, Brunetti and Vecchiocattivi 1993). Such processes are promoted by collisions of an open shell atom, electronically excited in an high energetic metastable state, with another atomic/molecular partner giving rise to the spontaneous emission of electrons accompanied by the formation of parent ions, aggregate ions and fragmentation ions. Therefore, the measure of the energy dependence of emitted electrons, also known as Penning Ionization Electron Spectra (PIES), provides direct information on the electronic rearrangements occurring within the collision complex, which directly correlates with the transition state of the autoionization processes. Moreover, molecular ionization probability and emitted PIES are strongly dependent on symmetry and energy of the atomic or molecular orbital from which the electron is extracted and then on their spatial orientation within the collision complex (Falcinelli *et al.* 2016a, 2016b).

Autoionization processes represent also barrier-less reactions, driven by an anisotropic optical potential, whose real part controls approach of reactants and removing of products, while the imaginary part triggers the passage from neutral reactants to ionic products through an electronic rearrangement. The investigation of these reactions is important for fundamental researches, to assess the coherentcontrol of reactive events at low temperature and then to explore the quantum nature of matter (Arango *et al.* 2006), and also for applied researchs, to exploit the soft ionization in the development of mass spectrometry technique and to prepare particular ionic clusters (de Zárate *et al.* 2019).

The Figure 1 shows a schematic view of the molecular beam apparatus operating in our laboratory (briefly presented in the next section) and depicts a metastable Ne^*atom, whose external electron is excited in the 3s orbital and its ionic core exhibits the same electronic configuration of the high electron affinity fluorine atom, that approaches to a water molecule. This event originates a collision complex where the spontaneous electron jump from one of HOMO orbitals of water to the ionic core of Ne^* releases enough energy to eject the 3s electron with a defined kinetic energy. Therefore, the measure of the energy dependence of emitted electrons, also known as Penning Ionization Electron Spectra (PIES), provides direct information on the electronic re-

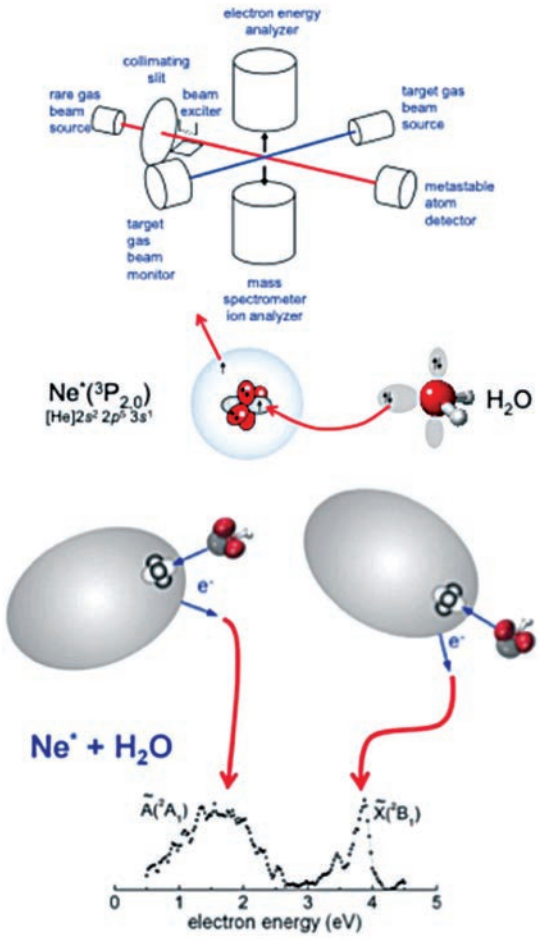

Fig. 1. *Upper panel*: A schematic view of the apparatus, where the primary beam of $Ne^*(^3P_{2,0})$ atoms, emerging from an electron bombardment supersonic seeded source, crosses at right angles the secondary beam of Kr atoms. PIES have been measured exploiting an hemispherical electron energy analyzer, while total, partial cross sections and branching ratios have been determined by the mass spectrometry technique.

Middle panel: A scheme of the atomic and molecular orbitals involved in the electron exchange.

Lower panel: A scheme of two different transition states leading to the formation of water ion in ground and excited states with the associated PIES.

arrangements occurring within the collision complex, which directly correlates with the transition state of the autoionization reaction. Moreover, molecular ionization probability and emitted PIES are strongly dependent on symmetry and energy of the molecular orbital from which the electron is extracted and then on the spatial molecular orientation within the collision complex, as depicted in Figure 1. We characterized in details such dependence for important hydrogenated molecules, as water, ammonia and hydrogen sulfide, and obtained results have been reported in (Falcinelli *et al.* 2016a, 2016b).

However, the dependence of the reaction probability on the valence orbital alignment of open-shell atoms still represents a basic open question. Recently (Falcinelli *et al.* 2018, 2019a, 2019b), our investigation has been focused on some prototype atom-atom reactions, as that involving Ne^*-Kr, in order to obtain information on this basic target. New insights on the stereodynamics of elementary processes involved are presented and discussed in the next section.

Results and Discussion

The experimental device used to investigate the dynamics of the auto-ionization reaction involving metastable Ne^*atoms and hydrogenated molecules or Kr atoms has been presented in details in Refs (Falcinelli et al 2016a, 2019a) and a schematic view is given in the upper part of Figure 1.

Shortly, it is a molecular beam (MB) apparatus, formed by a noble gas beam source from which the emerging Ne atoms are electronically excited by collisions with energetic electrons. The Ne^* MB crosses at right angles the MB of target species, which in recent experiments are noble gas atoms. PIES are measured by exploiting an hemispherical electron energy analyzer, while total, partial ionization cross sections and branching ratios (BRs), with their collision energy dependence, are obtained exploiting the mass spectrometry technique. In the present case, BRs of relevance are also those associated to the relative formation probability of the *parent ion* Kr^+ and of the ionic adductKr^+-Ne, also indicated as *associated ion*.

Results of recent experiments (Falcinelli *et al.* 2018, 2019a), performed at low collision energy and under high resolution conditions, permitted us to separate in measured PIES (left panel in Figure 2) the contributions of entrance and exit channels referred to specific spin-orbit levels of Ne^* reagent and of Kr^+ product, which are both open shell species. Moreover, PIES have been also

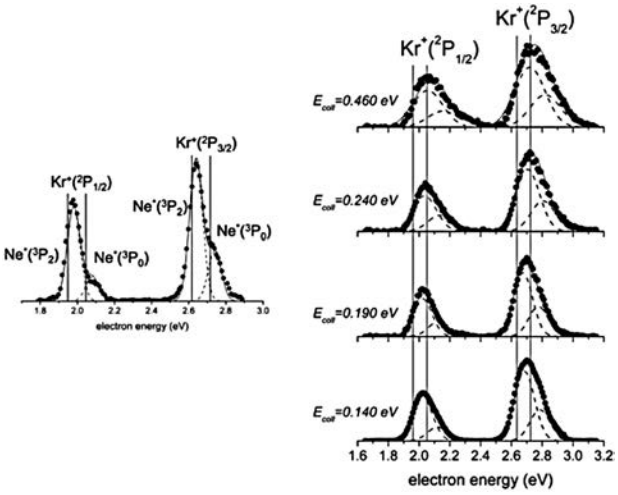

Fig. 2. *Left panel*: A Ne^*-Kr PIES measured at low collision energy (50 meV), where the contributions of four reaction channels, associated to two different spin-orbit states J of Ne^* neutral reactant (J_i=2,0) and of Kr^+ ionic product (J_f=3/2, 1/2), have been resolved. Vertical continuous lines represent the peak positions as predicted for the ionization of Kr by Ne(I) photons, and the shift of observed maxima in measured PIES relates to structure and stability of the reaction transition state. The peak area ratios, defining the relative reaction yields of the four channels, have been also evaluated through the analysis performed adopting four independent Gaussian functions with the same width (Falcinelli *et al.* 2018, 2019a).

Right panel: PIESs measured as a function of the collision energy (vertical lines as in the left panel). Their analysis (see caption of left panel) emphasizes the dependence of the peak position and of the peak area ratios on the collision energy.

measured as a function of the collision energy and obtained results are plotted in the right panel of Figure 2. Their analysis provided the dependences on the collision energy of the peak positions, related to the change of the transition state stability, and of the peak area ratios, determined by the change of relative reaction yields. These experimental findings, coupled with the ample phenomenology achieved in our laboratory on the anisotropic dynamical behavior of open-shell atoms (Pirani *et. al* 2006), suggested us that electronic rearrangements driving the reaction directly arise from polarization of external-floppy cloud of the 3s electron, charge transfer and modifications of angular momentum couplings of other valence electrons within the collision complex. Such rearrangements are accompanied by *adiabatic* and *non-adiabatic effects*, which play a crucial role in the control of the collision dynamics.

In particular, *adiabatic effects* mostly arise from strength and selectivity of configuration interaction which couples entrance and exit channels, having the same molecular symmetry and differing for one electron

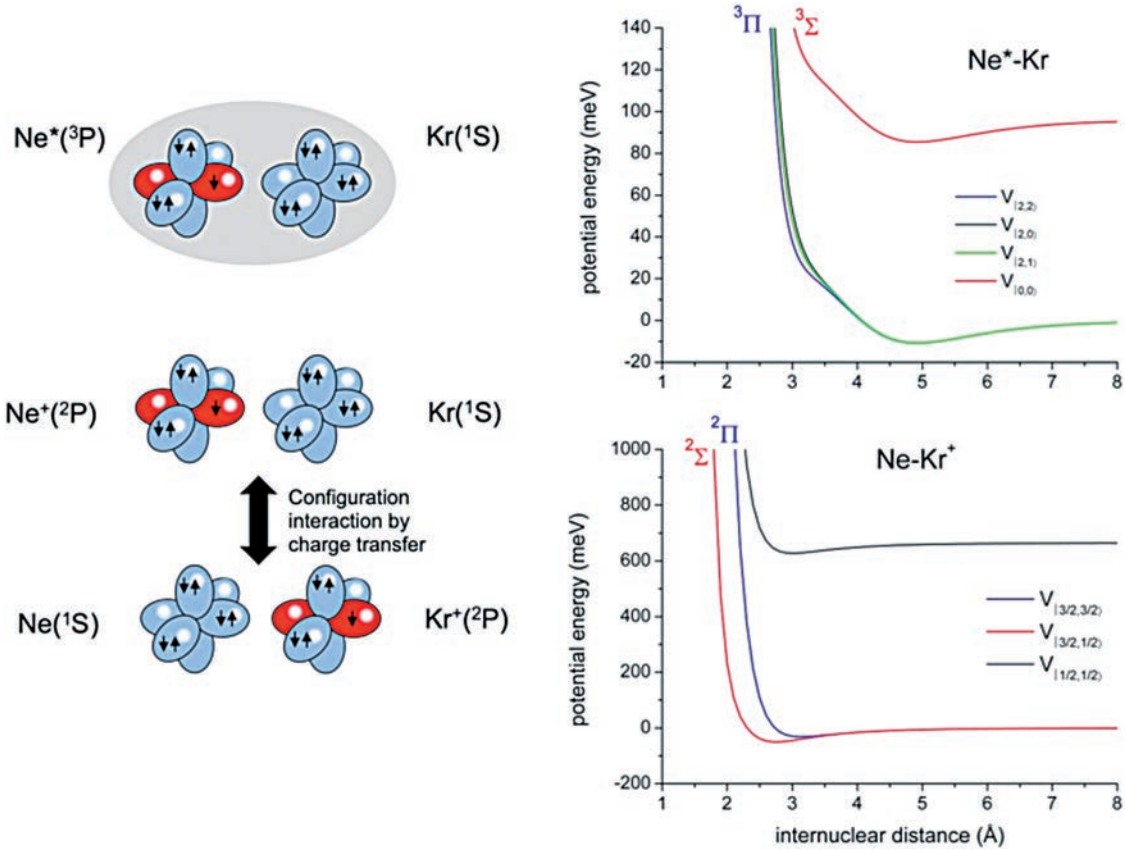

Fig. 3. *Left panel*: Representation of the configuration interaction, between states of entrance and exit channels differing for one electron exchange, which defines the CT contribution for Σ states. The corresponding component for Π states is much smaller (~1/5) (Falcinelli *et al.* 2019a) because of the reduced overlap integral between atomic half filled orbital exchanging the electron and aligned orthogonal to **R.**

Right panels: The real part of the optical potential *W* represented by adiabatic potential energy curves that are formulated in an internally consistent way for both entrance and exit channels, and indicated as $V|_{J,\Omega}>$. The interaction anisotropy at long range depends on the polarizability anisotropy of Ne^* atom and of Kr^+ ion, while, at intermediate and short range, it arises from anisotropic charge transfer (CT) contributions associated to configuration interaction between states differing for one electron exchange.

exchange (see left panel of Figure 3, where it is shown that in entrance channels most part of the anisotropy arises from the open shell nature of Ne^+ ion). They affect the anisotropic behavior of the real part of the optical potential and account for the adiabatic conversion of atomic states, defined in terms of $|J,\Omega>$ quantum numbers, where J represents the total electronic angular momentumof open shell species and Ω describes its projection along the inter-atomic direction, into molecular states of Σ and Π symmetry. The latter are emerging only at short separation distances, while the atomic states are representative of the system at large distances. Moreover, this conversion involves both entrance and exit channels and obtained interaction components are plotted in the right panel of Figure 3.

The imaginary components, defined in terms of quantum numbers proper of entrance and exit channels, are controlled by strength and radial dependence of *non-adiabatic effects.* They arise again from polarization, selective configuration interactions, changes in electron angular momentum couplings, spin-orbit and Coriolis contributions. Obtained components are plotted in the left panels of Figure 4.

The nature of the *non-adiabatic effects* suggests that the autoionization reaction occurs through two complementary microscopic mechanisms, illustrated in the right panel of Figure 4.

They are classified as:

i) direct mechanism: it is triggered by an homogeneous electron exchange, with coupling terms, between entrance and exit channels, called $A_{\Sigma\text{-}\Sigma}$ and $A_{\Pi\text{-}\Pi}$ on the basis of molecular character (Σ or Π) of initial and final state. The molecular character degrees of interest are given in upper right panel of Figure 4;

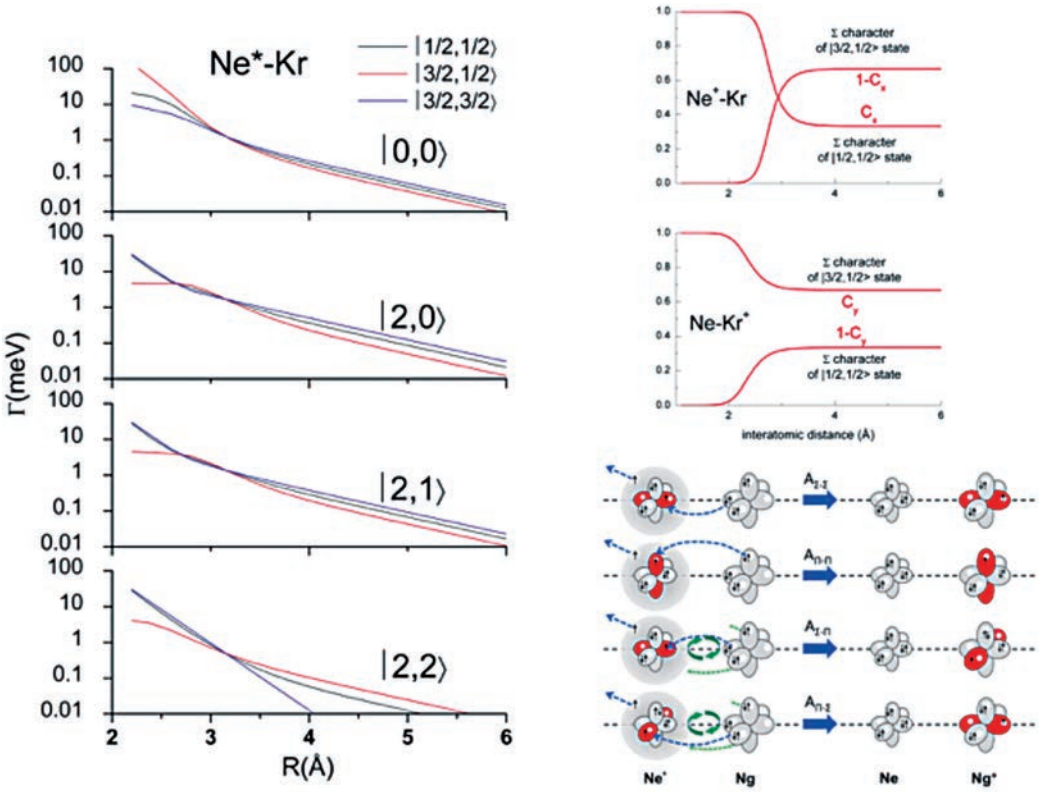

Fig. 4: *Left panel*: The state-to-state imaginary components Γ of the optical potential, defined in terms of $|J,\Omega>$ quantum numbers of Ne^* (^3P_J) reagent, with J=2 and J=0, and of $Kr^+(^2P_J)$ product, with J=3/2 and J=1/2.

Right upper panel: The radial dependence of the Σ character in entrance (C_x) and exit (C_y) channels, the Π character is defined as complement to 1 of the Σ one. All states accessible to the system are indicated by $|J,\Omega>$ quantum numbers. The |3/2,3/2> states are not included in the Figure since they exhibit a pure Π character at all interatomic distances.

Right lower panel: A cartoon representing the main features of direct (Σ-Σ, Π-Π) and indirect (Σ-Π, Π-Σ) mechanisms of autoinization processes, promoted by *non-adiabatic effects* operative during the collisions.

ii) indirect mechanism: it is stimulated by an heterogeneous electron exchange and it is accompanied by mixing/exchange between initial and final states of different symmetry. Such mechanism is basically promoted by spin-orbit polarization and Coriolis couplings effects.

It is important to note that the two mechanisms show a different radial dependence and therefore their relative role varies with the collision energy.

The interaction components, formulated as summarized above and plotted in Figures 3 and 4, permitted us to calculate within a semiclassical method (Brunetti and Vecchiocattivi, 1993) the state to state ionization cross sections in a wide collision energy range. Obtained results, plotted in Figure 5, exhibit rather different values and energy dependences. From these data, also BRs, defining the relative probability of selected channels, are here easily evaluable. This treatment provides, for the first time, an internally consistent rationalization of most relevant experimental findings, characterized with different techniques in various laboratories, that includes total and partial ionization cross sections, BRs and PIES.

Important observables are total ionization cross sections, reported some years ago (Gregor and Siska, 1981) and obtained, without any type of state selection, in a wide collision energy range. Some representative results are reported in Figure 5 as black points. A very good agreement between theoretical predictions and experimental data is obtained if present state-to state results are averaged over the statistical distribution of quantum states accessible in the Gregor and Siska experiment.

The energy dependence of BRs between selected reaction channels must also relate with the PIES measured in our laboratory and reported in Figure 2. BRs of interest for such a purpose are indicated in the upper part of Figure 6.

Preliminary results of *state to state* Associative/Pen-

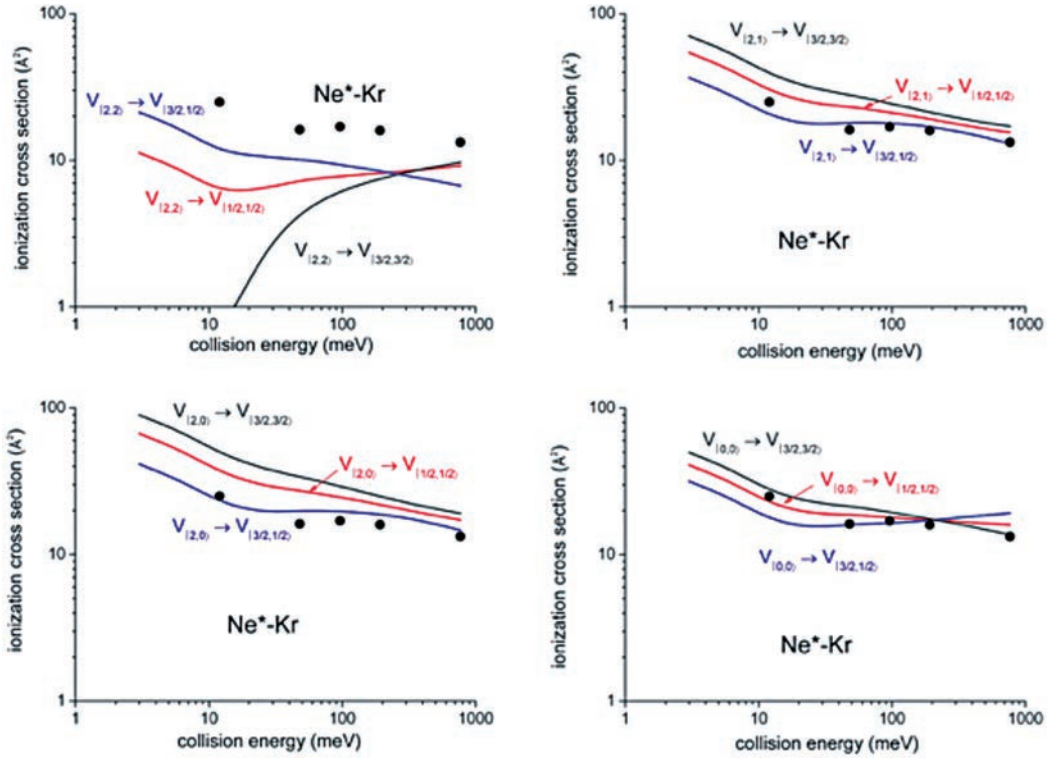

Fig. 5. State-to-state total ionization cross section determined for all allowed reaction channels as a function of the collision energy. The comparison with earlyresults (Greogor and Siska, 1981), reported as black points and referred to state averaged conditions, permits to emphasize differences in value and in energy dependence of state-to state results, while their statistical average is consistent with the experimental determination.

$$R_A = \frac{Q_{2,3/2}}{Q_{0,3/2}};\ R_B = \frac{Q_{0,1/2}}{Q_{0,3/2}};\ R_C = \frac{Q_{2,1/2}}{Q_{0,3/2}};\ R_A = \frac{Q_{2,1/2}}{Q_{2,3/2}};$$

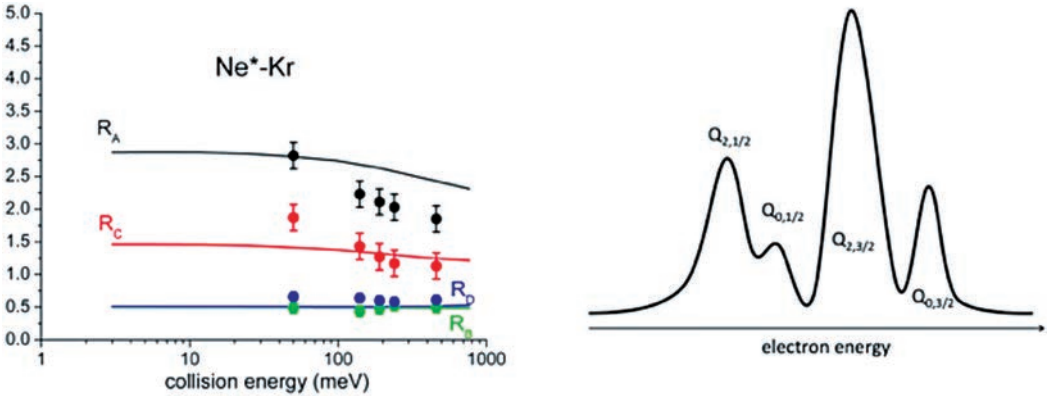

Fig. 6. *Left lower panel*: R_i values, representative of the cross section ratios of different channels $|J_i \rightarrow J_f\rangle$ respect to a reference one, as defined in the *upper part* of the figure. The continuous lines are the results of the present treatment carried out assuming a $^3P_2/^3P_0$ population ratio of about 3, as found for a Ne^* beam generated by electron impact (Brunetti and Vecchiocattivi, 1993). Points represent peak area ratios extracted from the analysis of PIES as depicted in the *right panel*.

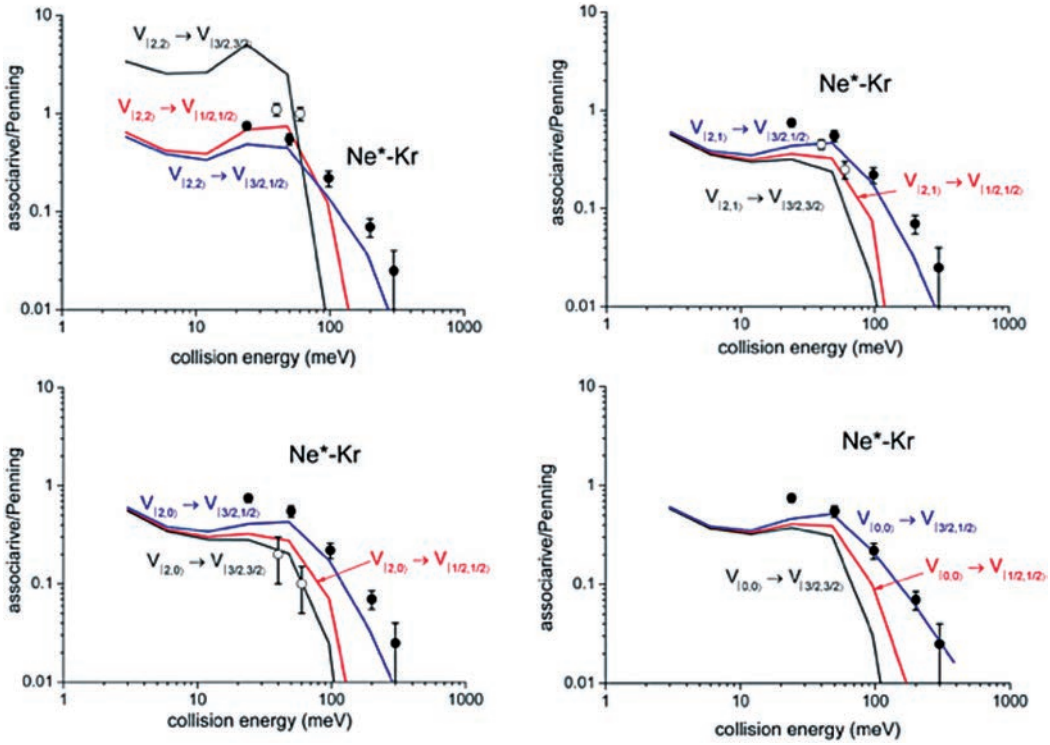

Fig. 7. Associative/Penning ratios predicted for all allowed reaction channels as a function of the collision energy. The comparison involves some hold experimental results (Brunetti *et al.* 1986), reported as black points and referred to state averaged conditions. Recent data (Zou *et al.* 2018), measured with $Ne^*(^3P_2)$ beams state selected in Ω=2,1,0 quantum states, are also reported (open circles) for a further important comparison since they represent the only data obtained under state selected conditions.

ning ratios, predicted as a function of the collision energy, are plotted in Figure 7 together with some experimental data (black points), measured some years ago in our laboratory without state selection (Brunetti *et al.* 1986). Again the experimental data compare well with the statistical average of present results. However, the most important and cogent comparison can be performed with recent data measured in the Losanna laboratory by Osterwalder group (Zou *et al.* 2018, Gordon *et al.* 2018). In such experiments the Ne^* beam has been state selected in J=2 and Ω=2,1,0 sublevels and important anisotropies in the reaction probability have been characterized, as shown by some representative data (open circles) reported in Figure 7: they appear to be consistent with the state to state selectivity predicted by the present treatment.

In conclusion, this new methodology provides unique information on the stereo-dynamics of *state to state* autoionization reactions. In this paper it is applied to a prototype atom-atom system, for which it allows to rationalize in a unifying picture most of the available experimental findings from our and other laboratories. The possibility to obtain *state to state* cross sections is of great interest for the investigation of quantum effects in the coherent control of collision processes, promoting Penning and associative ionization, from ultra cold up to thermal reactive collisions (Arango *et al.* 2006). Obtained results suggest also how to extend the methodology to autoionization reactions involving molecules (Jankunas*et al.* 2014, Falcinelli *et al.* 2016b), which are of great interest in several fields, including the balance of phenomena occurring in interstellar environments and planetary atmospheres. In addition, also electron-molecule impacts are of crucial relevance in many applications of molecular plasmas (Celiberto *et al.* 2009). It is of interest to emphasize that the microscopic dynamics of promoted dissociative electron attachment and resonant vibration excitations (Stibbe and Tennyson 1998, Celiberto *et al.* 2009), driven by a local complex potential, must be considered complementary to that of autoionization reactions.

Finally, the proposed microscopic mechanisms, driven by valence electron polarization, by changes in electron angular momentum couplings and by selective

charge transfer effects, all operative within the collision complex, are also of great relevance from a point of view of fundamental science. Specifically, they help to identify the role of electronic rearrangements determining the fate of the transition state of many other type of chemical processes, that are more difficult to characterize.

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