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An experimental and theoretical study of electronic excitation and charge transfer processes in collisions between $Cs(6^2S_{1/2})$ atoms and $Na^+(^1S_0)$ ions in the 0.30–4.00 keV energy range

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Abstract

The collisional system $Cs + Na^+$ with both species in their ground electronic state, has been studied using the crossed molecular beams technique and measuring the resulting fluorescent decay. Emissions from electronically excited $Cs(6^2P_{3/2})$ and $Cs(7^2P_{1/2,3/2})$ atoms have been detected as well as those from excited $Na(3^2P_{1/2,3/2})$ and $Na(4^2D_{3/2,5/2})$ produced by electron transfer. Cross-section values in the 0.30–4.00 keV energy range have been measured for the four different collision channels as well as the branching ratio between the resolved *J*-states for $Cs(7^2P_{1/2,3/2})$. A qualitative interpretation for some of the measured emission cross-sections as a function of the collision energy has been performed using ab initio one-electron calculations done for the (CsNa)⁺ quasimolecule. Hemiquantal dynamical calculations have been carried out at selected collision energies including radial and angular non-adiabatic couplings, comparing the calculated cross-sections with the experimental data. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Collisions between ions and neutrals (atoms or molecules) play an important role in different areas of the Physics and Chemistry of low density plasmas and ionised gases. Relevant examples of ionneutral processes are those taking place in interstellar clouds, planetary ionospheres, gas discharge and plasma deposition of thin metal films. Thus, ion-atom collisions are a current research topic in the field of Chemical Dynamics using molecular beams techniques. Their interest becomes even greater when both colliding particles are alkali atoms, since it is easy to generate the corresponding atomic beams and to measure the decaying fluorescence emission from electronically excited atoms, and also because their main

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dynamical behaviour can be studied performing relatively simple model calculations. Since the pioneering experimental work on alkali ion–alkali atom and alkali ion–atom systems done by Perel et al. [1–3], Aquilanti et al. [4–10], Tolk et al. [11], Andersen et al. [12], Østagaard et al. [13] and Brunetti et al. [14], covering many symmetric and asymmetric alkali ion–atom pairs, more elaborated experiments involving alkali atoms excited by polarised lasers to observe the specific alignment effects on electron transfer collisions have been done by Bähring et al. [15] and more recently by Thomsen et al. [16].

Taking into account the electronic structure of the alkali atoms it is not surprising that only the single ns valence electron becomes excited in the energy range currently under study. Then, results on theoretical calculations can be obtained using relatively simple models which take into account the intrinsic non-adiabatic nature of the electronic excitation or electron transfer processes. Aquilanti [17] improved on earlier studies of Perel et al. [2], Melius et al. [18] and McMillan [19]. Shingal et al. [20] performed semiclassical studies while more recently Nakamura et al. [21] reported on a complete picture of the two-state curve crossing problems which can be applied to elastic and inelastic scattering as well as to perturbed bound state problems.

A systematic study of collisions involving alkali ions and alkali atoms [22-29] was done in our research group from both experimental and theoretical points of view. One-electron ab initio calculations using non-empirical relativistic pseudopotentials to model the core electrons have been successfully applied to several alkali ionatom pairs allowing an interpretation of the most relevant experimental results. In this paper we report on the results obtained for the $Cs + Na^+$ collisional system. The paper is organised as follows: a brief description of the experimental apparatus is contained in Section 2, while Section 3 is devoted to present experimental results. A discussion of the obtained data in terms of simple dynamical models as well as on our recent ab initio calculations performed on the (CsNa)⁺ quasimolecule is presented in Section 4. Dynamical calculations performed in the framework of the hemiquantal dynamics are given in Section 5 and conclusions are summarised in Section 6.

2. Experimental setup

As a detailed description of the experimental crossed beam setup has been given already in [22,29], here we will limit to briefly describe its most relevant features. In this apparatus a beam of alkali ions (Na⁺ in the present case) is generated by a thermionic source and accelerated by a 0.10-4.00 keV electric field, focused by an einzel lens system and later collimated. The ion beam crosses at right angle the thermal neutral beam of $Cs(^2S)$ atoms generated by the displacement reaction in solid phase $Ba(s) + 2CsCl(s) \rightarrow BaCl_2(s) + 2Cs$ (g), which takes place in a heated oven. The fluorescence emitted by decay of the excited electronic states produced in the collision is collected by an optical system placed perpendicularly to the collision plane at the scattering center, analysed by a 50 cm monochromator and read by a photomultiplier.

Background pressure is usually maintained in the range 10^{-7} – 10^{-6} mbar during experiments. Recently, the experimental setup has been improved by installing a computerised data-collection system which both shows on the screen the fluorescence spectrum and accumulates the average fluorescence intensity measured along a given time interval.

In order to report absolute cross-section values, experiments on the Cs + e⁻ system were done to calibrate our experimental system [30]. To this end, cross-sections for the inelastic process Cs($6^2S_{1/2}$) + e⁻ \rightarrow Cs($6^2P_{1/2,3/2}$) + e⁻ were measured in arbitrary units and then compared with previously reported data [31] in absolute units.

3. Experimental results and discussion

3.1. Total and state-to-state cross-sections

When cesium atoms in their ground electronic state collide with sodium ions, different excited electronic states of the target Cs atom can be populated by direct excitation as well as those of sodium atoms by an electron transfer processes. Emissions for the following decay processes have been observed and their total emission cross-section determined at different collision energies:

(a)
$$Cs(6^2S_{1/2}) + Na^+({}^{1}S_0)$$

 $\rightarrow Cs(6^2P_{1/2,3/2}) + Na^+({}^{1}S_0)$
 $Cs(6^2P_{3/2}) \rightarrow Cs(6^2S_{1/2}), \quad \lambda = 8521.1 \text{ Å}$

(b)
$$Cs(6^2S_{1/2}) + Na^+(^1S_0)$$

 $\rightarrow Cs(7^2P_{1/2,3/2}) + Na^+(^1S_0)$
 $Cs(7^2P_{1/2,3/2}) \rightarrow Cs(6^2S_{1/2}),$
 $\lambda = 4593.2, 4555.4 \text{ Å},$

(c)
$$Cs(6^2S_{1/2}) + Na^+({}^1S_0)$$

 $\rightarrow Cs^+(6^1S_0) + Na(3^2P_{1/2,3/2})$
 $Na(3^2P_{1/2,3/2}) \rightarrow Na(3^2S_{1/2}),$
 $\lambda = 5895.9, 5889.9 \text{ Å},$

$$\begin{array}{ll} (d) & Cs(6^2S_{1/2}) + Na^+(^1S_0) \\ & \rightarrow Cs^+(6^1S_0) + Na(4^2D_{3/2,5/2}) \\ & Na(4^2D_{3/2,5/2}) \rightarrow Na(3^2P_{1/2,3/2}), \\ & \lambda = 5688.2, 5682.7 \ \text{\AA}. \end{array}$$

The electronic state of the excited alkali atom can be characterised by the total electronic angular momentum J and decay emissions to lower energy states involving different J' values are possible. In this paper we report state-to-state cross-sections $\sigma(J' \leftarrow J)$ for the excitation processes (b) while only total emission cross-sections (summed over all possible J and J' values) are reported for processes (a), (c) and (d).

3.2. Target excitation processes: $Cs(6^2S_{1/2}) + Na^+({}^{1}S_0) \rightarrow Cs(6^2P_{1/2,3/2}) + Na^+({}^{1}S_0), Cs(7^2P_{1/2,3/2}) + Na^+({}^{1}S_0)$

The collision channel involving electronic excitation of the target atom $Cs(6^2S_{1/2})$ to the first excited states in collisions with sodium ions produces caesium atoms in the levels $6^2P_{1/2}$ and $6^2P_{3/2}$ which decay to the ground level $6^2S_{1/2}$ by fluorescent emission at 8943.5 and 8521.1 Å, respectively. These both lie in the infrared zone of the spectrum, where background noise from our beam sources is highest, which makes them difficult to characterise in our experimental setup. Consequently, the measurement of the cross-section has been possible only for the more energetic $Cs(6^2S_{1/2}) \leftarrow Cs(6^2P_{3/2})$ transition.

Total emission cross-sections for the $Cs(6^2S_{1/2})$ + $Na^+({}^1S_0) \rightarrow Cs(6^2P_{3/2}) + Na^+({}^1S_0)$ process as a function of the collision energy in the laboratory frame (LF) in the 0.70–2.50 keV energy range are given in Fig. 1 together with the error bars reflecting experimental uncertainty. The low signalto-noise ratio limited the observable threshold energy down to 0.70 keV in the LF.

Since no other electronic excitations leading to excited states of Cs decaying to the $6^2P_{3/2}$ level have been observed, cascade effects can be neglected. LF emission cross-section values obtained for the excitation process under consideration lie in the same range as those previously found for the systems Na–Na⁺ and Rb–Na⁺ in our group [22,25], and for the K–Na⁺ system measured by Aquilanti et al. [8]. Cross-section values at 1000 eV in the LF in the serie K, Rb, Cs against Na⁺ are



Fig. 1. Emission cross-sections versus LF (E_{lab}) and CMF (E_{CM}) collision energies for the formation of Cs($6^2P_{3/2}$) in collisions between Cs($6^2S_{1/2}$) and Na⁺(1S_0).

 6.5×10^{-17} , 5.5×10^{-16} and 6.2×10^{-16} cm², respectively, where for the last one the $6^2 P_{1/2}$ contribution cannot be included. According to these results we can conclude that translational energy in the LF becomes more effective in promoting direct electronic excitation of target atoms to their first excited level as their mass increase (the Na–Na⁺ system, for which direct excitation and electron transfer processes are resonant has not been included). In the simplest way this effect can be justified taking into account that available collisional energy in the center of mass frame (CMF) increases from K to Cs, thus increasing the process probability in the range of energies considered.

Another target excitation process also detected under our experimental conditions for the Cs–Na⁺ system, leads to excited Cs($7^2P_{1/2,3/2}$). In this case it is possible to characterise fluorescent emissions at 4593.2 Å (from Cs($6^2S_{1/2}$) \leftarrow Cs($7^2P_{1/2}$)) and at 4555.4 Å (from Cs($6^2S_{1/2}$) \leftarrow Cs($7^2P_{3/2}$)) separately, allowing state-to-state cross-sections to be determined. In Fig. 2 total emission cross-sections for Cs($7^2P_{1/2,3/2}$) formation as a function of the collision energy in the LF are plotted in the 0.50– 3.00 keV energy range. LF energy dependence of the state-to-state branching ratio emission crosssections $(\sigma(J' = 1/2 \leftarrow J = 3/2) / \sigma(J' = 1/2 \leftarrow J =$ 1/2), where J' and J stand, respectively, for the final and initial atomic total electronic angular momentum involved in the transition) is given in Fig. 3. As it can be seen in Fig. 3 the branching ratio is strongly energy dependent, varying from about 0.4 at low collision energies to values between 1.5 and 1.8 at the highest ones. All these values are lower than the statistical result of 2, with the collision exit channel producing $Cs(7^2P_{3/2})$ being favoured when collision energy increases, while that leading to $Cs(7^2P_{1/2})$ is essentially energy-independent as it has been found from the measured $\sigma(J' = 1/2 \leftarrow J = 1/2)$ state-to-state cross-section [30]. Moreover, in Fig. 3 we can appreciate some kind of structure, particularly in the high collision energy range, which could be attributed to interference effects, but the uncertainty of the measured state-to-state cross-sections does not allow an interpretation of these oscillations. A similar branching ratio dependence, with more pronounced oscillations, was found in the Rb-Cs⁺ [27] collision system but for the electron transfer channel leading to $Cs(6^2P_{1/2,3/2}).$





Fig. 2. Total emission cross-sections versus LF (E_{lab}) and CMF (E_{CM}) collision energies for the formation of Cs($7^2P_{1/2,3/2}$) in collisions between Cs($6^2S_{1/2}$) and Na⁺(1S_0).

Fig. 3. Cross-section branching ratio between processes leading to $Cs(7^2P_{3/2})$ and $Cs(7^2P_{1/2})$ in collisions between $Cs(6^2S_{1/2})$ and $Na^+(^1S_0)$ as a function of the LF (E_{lab}) and CMF (E_{CM}) collision energies.

3.3. Electron transfer processes: $Cs(6^2S_{1/2}) + Na^{+(^{1}S_0)} \rightarrow Cs^{+}(6^{^{1}S_0}) + Na(3^2P_{1/2,3/2}), Cs^{+}(6^{^{1}S_0}) + Na(4^2D_{3/2,5/2})$

Total emission cross-sections (where contributions from J = 1/2 and J = 3/2 levels of excited Na atoms are considered together) as a function of the collision energy in the LF for the exit channel producing Na($3^{2}P_{1/2,3/2}$) in the 0.30–3.50 keV energy range are shown in Fig. 4. This is the most important channel in $Cs + Na^+$ collisions. For it, absolute cross-section values are about two orders of magnitude higher than those for the fundamental electronic transition $(6^2 S_{1/2} \leftarrow 6^2 P_{1/2,3/2})$ for Cs atoms and also somewhat higher than the emission cross-section values obtained previously for equivalent electron transfer process in the $Rb(5^2S_{1/2}) + Na^+({}^1S_0)$ collision system [25]. This fact can be qualitatively interpreted considering that Cs is more readily polarised than Rb (when both are in the ground state), which facilitates the target valence ns¹ electron transfer to the impinging ion Na⁺.

A quantitative interpretation of the experimental data for the $Cs(6s^1)$ to $Na(3p^1)$ electron



Fig. 4. Total emission cross-section for the electron transfer process leading to $Na(3^2P_{1/2,3/2})$ versus LF (E_{lab}) and CMF (E_{CM}) collision energies in collisions between $Cs(6^2S_{1/2})$ and $Na^+(^1S_0)$ corrected by the cascade effect from $Na(4^2D_{3/2,5/2})$ decay.

transfer can only be achieved by performing full dynamical calculations including the manifold of electronic potential energy curves correlating with the asymptotic atomic states and taking into account all non-adiabatic couplings between them. Nevertheless, to give a qualitative interpretation of the experimental results, simple models can also be useful. To this end, experimental data have been fitted to the linear two-state Landau-Zener-Stuckelberg (LZS) model [32]. In Fig. 4 continuous lines represent the best fitting of the experimental excitation function to this model for a rotationally coupled Σ - Π transition. It can be seen that this model can reproduce well the experimental data, but a proper fit of the cross-section values for the whole energy range requires two different sets of parameters for the corresponding LZS equation. According to this simple model, the electron transfer process $Cs(6^2S_{1/2}) + Na^+({}^1S_0) \rightarrow$ $Cs^+(6^1S_0) + Na(3^2P_{1/2,3/2})$ can be easily interpreted as being controlled by a rotational nonadiabatic coupling between an entrance channel of Σ^+ symmetry, correlating asymptotically with $Cs(6^2S_{1/2}) + Na^+(^1S_0)$, and an exit one of Π symmetry and correlating with product $Cs^+(6^1S_0) + Na(3^2P_{1/2,3/2})$, with the asymptotically degenerated Σ^+ channel playing a minor role. However, the limitations of the model are evidenced by its inability to describe adequately the cross-section energy dependence in the whole energy range. This was to be expected considering the manifold of electronic states involved along the collision. In fact, any charge transfer or target excitation along the collisional event produces a mixture of the different electronic states that can be associated with the quasimolecule formed by the collisional partners.

The second electron transfer process measured is $Cs(6^2S_{1/2}) + Na^+ ({}^1S_0) \rightarrow Cs^+(6^1S_0) + Na (4^2D_{5/2,3/2})$ where the produced excited atoms $Na(4^2D_{3/2,5/2})$ decay to the lower energy level $Na(3^2P_{1/2,3/2})$. Its total emission cross-section as a function of the LF collision energy in the range 0.50-2.00 keV is given in Fig. 5. Values for this $Na(4^2D_{3/2,5/2}) \leftarrow Na(3^2P_{1/2,3/2})$ transition have been taken into account in the calculation of the emission cross-section associated with the formation of $Na(3^2P_{1/2,3/2})$ to correct it for the cascade



Fig. 5. Total emission cross-section for the electron transfer process leading to Na($4^2D_{3/2,5/2}$) as function of the LF (E_{lab}) and CMF (E_{CM}) collision energies in the Cs + Na⁺ collisional system.

effect. Absolute cross-section values for this process are about one order of magnitude lower than those measured for the Na($3^2P_{1/2,3/2}$) formation and about one order higher than emission crosssections for the equivalent electron transfer process in the Rb + Na⁺ system. While the fitting is not so good as for the previously considered $3p \leftarrow 3s$ transition, the experimental excitation function can be described by the LZS model (not shown in Fig. 5) considering a Σ - Σ non-adiabatic coupling between the Σ^+ entrance channel correlating asymptotically with colliding particles and the Σ^+ component exit channel correlating with collision products $Cs^+(6^1S_0) + Na(4^2D_{3/2.5/2})$.

4. Ab initio calculations for the (Cs–Na)⁺ collisional system

In order to improve our understanding at atomic level of the mechanism leading to excited states of both Cs and Na atoms, we have to get information on all the potential energy curves describing interactions between the collision partners as well as on the non-adiabatic couplings between them. Even with the continuously increasing supercomputational facilities nowadays available, high level and full ab initio calculations for ground and excited states of the $(Cs-Na)^+$ system which include all electrons are still too expensive. However, for systems like the present one we can take advantage of the pseudo-monoelectronic character of the quasimolecule formed along the collision using pseudopotential techniques [33], which we have already applied to other systems [25,27,29] providing a good qualitative interpretation of the measured data. In the present case, non-empirical pseudopotentials derived by Durand and Barthelat [34] have been used to replace sodium (1s2s2p) and caesium (1s2s2p3s3p4s3d4p5s4d5p) electron cores, including also relativistic parameters for the latter [35]. Then, adiabatic potential energy curves have been calculated using a restricted open-shell Hartree-Fock (ROHF) technique. Because of the high polarizability of the atoms involved, the calculations were performed considering the core-valence correlation by including a core polarisation potential (CPP) in the Fock operator using a formalism proposed by Foucrault et al. [36].

Since the $(Cs-Na)^+$ system involves large cores and in our collision energy range the colliding particles can approach each other within less than 1 Å, the core–core repulsion has not been calculated as a pure coulombic value, but as the energy difference between the CsNa²⁺ and Na⁺ and Cs⁺ in an all-electron calculation with a minimal basis set [37,38]. The single valence electron has been described by extended Gaussian type orbitals (GTO) basis sets: [7s, 6p, 5d, 2f/5s, 5p, 4d, 2f] for Na [39] and [7s, 6p, 6d, 2f/6s, 6p, 5d, 2f] for Cs [40]. Energy calculations were performed at internuclear distances (*R*) ranging from 1.00 to 50.00 a.u.

Using this GTO basis set, 37 adiabatic potential energy curves corresponding to 56 molecular states have been calculated with high reliability. These curves correlate asymptotically with atomic states, whose energy diverge from the corresponding experimental values by 1% or less. According to their symmetry the 37 adiabatic curves considered are distributed as follows: $18\Sigma^+$, 12Π , 6Δ and a single Φ , and they describe the asymptotic neutral atomion pair (Cs + Na⁺ or Cs⁺ + Na) states in which the Cs and Na atoms have electronic configurations ranging from (of ordered increasing energies) Cs(6s¹) to Cs(7d¹) and Na(3s¹) to Na(5p¹), respectively. For clarity reasons, only those calculated potential energy curves whose asymptotical electronic configuration lies in the energy range bounded by the fundamental ($Cs^+ + Na(3s^1)$) and the most excited one observed experimentally ($Cs^+ + Na(4d^1)$) are given in Fig. 6.

Sometimes a qualitative interpretation of the experimental excitation functions can be given in terms of the energy evolution of the adiabatic molecular orbitals (MOs) as a function of *R*. This is the case of the electron transfer process $Cs(6^2S_{1/2}) + Na^+(^1S_0) \rightarrow Cs^+(6^1S_0) + Na(3^2P_{1/2,3/2})$ whose cross-section-energy dependence has been discussed previously in terms of a rotationally non-adiabatic LZS model. In Fig. 7 the electronic



Fig. 6. Adiabatic potential energy curves for the $(CsNa)^+$ ionic system versus internuclear distances (R) obtained by ab initio calculations (see text). Continuous lines (-----) stand for Σ^+ states, dotted lines (----) stand for Π^+ and dot-dash ones (-----) stand for Δ states. Only energy curves for asymptotical ionatom states whose energy lies between the ground Cs^+ + $Na(3s^1)$ electronic configuration and the excited Cs^+ + $Na(4d^1)$ one are shown.



Fig. 7. Evolution of the lowest adiabatic MOs as a function of internuclear distance for the $Cs + Na^+$ collisional system.

energy (without the core-core repulsion) evolution is given as a function of R for the adiabatic MOs correlating with the ground state (1σ) , the entrance channel (2 σ) and the exit ones (3 σ and 1 π) asymptotically degenerated. It can be seen how the entrance channel 2σ crosses the exit channel 1π (correlating with $Cs^+ + Na(3p^1)$) at about 7.50 a.u. After this, the 2σ comes very close to the 1π at about 2.50 a.u., and for lower R-values both MOs evolve practically in parallel. The 3σ exit channel (also correlating with $Cs^+ + Na(3p^1)$) runs energetically very separated from the entrance channel (2σ) , both MOs evolving also in a parallel way at very short (below 2.00 a.u.) internuclear separations. The $2\sigma - 1\pi$ crossing justifies the rotational non-adiabatic LZS fit at low and middle collision energies, then allowing to interpret the experimental data as dominated by the mentioned crossing and in terms of a two states model. As collision energy increases, atomic cores can approach closer and then non-adiabatic transitions $2\sigma - 1\pi$ can also take place at R = 2.50 a.u. or less. This behaviour can justify the good fit, at least qualitatively, but the basic inadequacy of such a two states model also becomes evident as ought to be expected considering the manifold of potential energy curves which can be explored along the

collision process and which play an important role in the population of the atomic states. For instance, let us consider the charge transfer process leading to Na(4d¹) + Cs⁺ whose excitation function can be acceptably fitted using a radial LZS model. An analysis (not reported here) of the evolution of the adiabatic MOs 14 σ , 8 π and 4 δ correlating with Na(4d¹) and 2 σ for the entrance channel along *R*, shows no crossings between them in all the range of internuclear separation. It is then clear that any interpretation, even qualitative, requires more elaborated models [21,41] or dynamical calculations.

5. Dynamical calculations

As has been stated before, in collisional systems like the $(CsNa)^+$ and even at the lowest experimental energies, we must consider all the electronic states that can be populated along the collision. Dynamical calculations require to know both the evolution of the electronic states and all couplings between them. In the framework of the adiabatic representation [42] the Born-Oppenheimer electronic hamiltonian matrix is diagonal, the electronic excitation being induced by nuclear motions. Then the corresponding non-adiabatic couplings between the different adiabatic electronic states must also be calculated. According to the ab initio calculations reported in the previous section we have obtained 56 electronic states (corresponding to 37 adiabatic potential energy curves) asymptotically very well described among a manifold of 127 electronic states. Non-adiabatic couplings for these states have been calculated from the set of adiabatic electronic wave functions $\{\Phi_i\}$ *R*-dependents. For the present case of two colliding particles [43] we need to calculate the so-called radial and rotational couplings matrix elements given by $\langle \Phi_i | \partial \partial R | \Phi_i \rangle$, $\langle \Phi_i | \hat{L}_v | \Phi_i \rangle$, respectively, where \hat{L}_v is the y-component of the orbital angular momentum operator in the rotating frame. These matrix elements were evaluated numerically [44] using the finite differences method on a grid of points along *R* and interpolated using a cubic spline method.

Dynamical calculations for the $(CsNa)^+$ colliding system have been performed in the frame-

work of hemiquantal mechanics [45] using a computer code implemented by us in our computational facilities. In this method the collision evolution of the electronic quantum degrees of freedom is described by the time-dependent Schrödinger equation for the complete electronic wave function Ψ . This function is expanded in a set of the adiabatic molecular electronic wave functions previously obtained $\Psi = \sum_i c_i(t)\Phi_i$ where complex coefficients $c_i(t)$ are function of time t (or, equivalently, a function of R, provided that R is a function of time). The remaining degrees of freedom, which describe nuclear motion (in the CMF) in terms of the polar coordinates (R, Θ) , evolve according to the four differential coupled hemiquantal equations for \dot{R} , Θ , \dot{p}_R and \dot{p}_{Θ} . For any particular collision, the set of hemiquantal equations describing the nuclear motion is solved together with the electronic time-dependent Schrödinger equation, which involve both the radial and rotational non-adiabatic couplings [46]. In the hemiquantal approach the accuracy of the results is limited by that of the potential energy curves and non-adiabatic couplings, as well as by the number of adiabatic molecular states used in the adiabatic expansion of Ψ .

In the range of the collision energies studied, the orbital angular momentum (1) of the ion-atom system can reach very high values. On the other hand, changes in the projection of the total electronic orbital angular momentum are small and the total electronic spin is conserved in any collision. Thus, the total angular momentum K of the system is given by $K \simeq l$. In order to calculate collision cross-sections, the coupled set of classical and quantum degrees of freedom of the system are solved for a fixed set of initial conditions: relative position (R_0) , initial electronic entrance channel $c_{init}(t_0)$, collision orbital angular momentum (l) (or the equivalent classical impact parameter) and collision energy (E). All hemiquantal trajectories start at $R_0 = 50.00$ a.u. where interactions are negligible and the initial electronic state is the second Σ^+ one correlating with the experimental $Cs(6^2S_{1/2}) + Na^+(^1S_0)$ entrance channel. At fixed collision energies, cross-section values are obtained until convergence on l. The $c_i(t)$ coefficients involved in the complete electronic wave function expansion are *l*-dependent as is also the calculated transition probability from the initial state (*i*) to any possible exit channel (*f*) at the end of the hemiquantal trajectory $(t \rightarrow \infty)$. Then total transition probability is given by

$$P_{f\leftarrow i}^{l}(E) = |c_f(l,\infty)|.$$
(1)

Total inelastic excitation and/or electron transfer cross-sections are given by the well-known equation

$$\sigma_{f \leftarrow i}(E) = \frac{\pi}{2\mu E} \sum_{l=0}^{l_{\max}} (2l+1) |c_f(l,\infty)|^2,$$
(2)

where μ is the reduced mass of $(Cs-Na)^+$ and l_{max} the maximum collision orbital angular momentum leading to non-zero probabilities for the process considered.

5.1. Results and discussion

In order to obtain the most accurate results possible with our computational facilities and CPU time allowances, the adiabatic expansion has been performed over the 18 lowest energy ${}^{2}\Sigma^{+}$ states and the 12 lowest ${}^{2}\Pi$ ones of the (CsNa)⁺ system, the corresponding dynamical calculations being carried out for eight collision energies in the low range of experimental data. From a detailed analysis of the collision time evolution of the complete electronic wave function for a selected number of hemiquantal calculations, some general trends have been observed which are essentially independent either of the collision orbital angular momentum or of the energy. It can be appreciated that non-adiabatic interactions appear at distances R as large as 35-30 a.u., causing a mixture of different excited Σ or Π states. The time contribution to these states oscillates with individual values, usually reaching their maximum at R values ranging from 20 a.u. to their corresponding turning point. In the second half-collision, when both nuclei are receding apart, a similar oscillatory contribution from each state also appears, the corresponding coefficients becoming stabilised at some R about 25–30 a.u. At a fixed collision energy, oscillatory behaviour for each electronic state contribution is strong and sharp for low values of l but these oscillations become both reduced in intensity and smoothed for high l values. This behaviour could be explained considering that the collision orbital angular momentum introduces a centrifugal potential whose effect is to preclude partially the participation of the excited states at short distances, thus making a particular excitation contribution less favourable. At fixed collision energies (E) and for a given electronic transition, the total transition probability (Eq. (1)) is a function only of the orbital angular momentum P(l). In Fig. 8 are given (for a CMF collision energy of 425 eV) the opacity functions $P(l) \cdot (2l+1)$ for the $Cs(6s^1)$ excitation to $Cs(7p^1)$ correlating with both quasimolecular states 10 ${}^{2}\Sigma^{+}$ and 6 ${}^{2}\Pi$, and for the formation of Na(3p¹) correlating with 3 $^{2}\Sigma^{+}$ and 1 ${}^{2}\Pi^{+}$ and induced by collisions between Cs(6s¹) and $Na^+(3s^0)$. Since these excited Cs and Na atoms can be produced both by radial and rotational nonadiabatic coupling, the contributions to the total opacity function are shown separately. The figure shows the oscillatory behaviour of the opacity functions that was to be expected from the quantum mechanical solutions of the quantum degrees of freedom (the electronic subsystem). For these transitions at the specified collision energies, the opacity functions are fully converged for a maximum *l* value of 25.500 a.u. Both $\Sigma^+ - \Sigma^+$ opacity functions show similar behaviour, their probabilities being of the same order of magnitude and very low for l < 5.000 a.u. In the case of the $\Sigma^+ - \Pi$ opacity functions for the charge transfer process leading to $Na(3p^1)$ only large impact parameters (for l > 10.000 a.u.) are found to give an important contribution, while for the Cs excitation leading to $Cs(7p^1)$ all impact parameter values contribute, but their probabilities are lower by one order of magnitude or more that those involved in the charge transfer discussed previously. Similar qualitative behaviours have also been observed for other collision energy values.

Total cross-sections for all different collision channels involved in the adiabatic expansion of the complete electronic wave function have been obtained by hemiquantal calculations at different CMF collision energies. In Table 1, it can be seen the $l_{\rm max}$ values at the selected collision energies, together with the total cross-sections obtained



Fig. 8. Opacity functions $P(l) \cdot (2l+1)$ (see text) at 425 eV CMF collision energy for target excitation (to Cs(7p¹)) and electron transfer (to Na(3p¹)) processes from reactants in their ground electronic state. Lower panel: $\Sigma^+ - \Sigma^+$ and $\Sigma^+ - \Pi$ opacity function components leading to Cs(7p¹) + Na⁺ correlating with both the $10^{2}\Sigma^+$ and the $6^{2}\Pi$ quasimolecular states. Upper panel: $\Sigma^+ - \Sigma^+$ and $\Sigma^+ - \Pi$ opacity function components leading to Cs(7p¹) + Na⁺ correlating with both the $10^{2}\Sigma^+$ and the $3^{2}\Sigma^+$ and the $1^{2}\Pi$ quasimolecular states.

Table 1

Hemiquantal calculated cross-sections and l_{max} values for the formation of different asymptotic atomic states of Cs and Na in collisions between Cs and Na⁺ in their respective electronic ground states

$E_{\rm CMF}~({\rm eV})$	l _{max} (a.u.)	$\sigma(\mathrm{Cs}(6\mathrm{p}^{1-2}\mathrm{P}))$	$\sigma(\mathrm{Cs}(7\mathrm{p}^{1-2}\mathrm{P}))$	$\sigma(\mathrm{Na}(3\mathrm{p}^{1-2}\mathrm{P}))$	$\sigma(\mathrm{Na}(\mathrm{4d}^{1-2}\mathrm{D}))$	$\sigma(\mathrm{Na}(\mathrm{3d}^{1-2}\mathbf{D}))$
425	25,500	1.25	0.91	2.40	0.807	4.09
600	32,400	1.77	1.22	3.04	1.28	6.76
770	39,100	1.95	1.38	3.16	2.32	7.74
850	43,800	2.07	1.47	3.29	2.73	8.06
1025	50,200	2.45	1.46	3.24	3.47	8.33
1195	54,000	2.68	1.51	3.19	4.06	8.11
1275	57,000	2.89	1.65	3.30	4.50	8.09

Cross-section values have to be multiplied by 10^{-15} and given in cm².

from Eq. (2) for the experimentally observed exit channels as well as for the channel leading to $Na(3d^{1/2}D)$.

We must proceed carefully before comparing calculated and experimental cross-section values. At a given collision energy from hemiquantal cal-

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culations, cross-section for the formation of a given atom (Cs or Na) in a well-defined state is obtained independently of the final measured property which characterises this final atomic state. Moreover, the number of possible final states and the calculated transition probabilities are limited by the adiabatic expansion done. Experimentally, at the same collision energy a large number of both excited target Cs states and excited Na ones (formed by electron transfer) are open, and they have not been included in the adiabatic expansion of the complete electronic wave function. In addition, some states can decay to lower energy ones, producing either a cascade effect or decaying to other excited states which are not characterisable experimentally. Consequently, some limitations can appear in the comparison of calculated cross-section with experimental emission cross section data.

In the case of calculated cross-section leading to $Cs(6p^{1/2}P_{1/2,3/2})$, for which the spin-orbit interaction has not been included, results cannot be directly compared with experimental data since only the J = 3/2 component of the $C_{s}(6p^{1/2}P_{1/2,3/2})$ energy levels has been measured. Calculated cross-section values can be expected to be larger than measured data considering that they include all the states for the spectral term $C_{s}(6p^{1} P)$ and this agrees quite well with the data shown in Fig. 9(a). In a first approximation, and assuming that the cross-section branching ratio for J = 3/2 and J = 1/2 level components is statistical, excitation cross-section leading to Cs $(6p^{1} {}^{2}P_{3/2})$ can be obtained and is also represented in Fig. 9(a) where it can be seen that, although the corresponding absolute values are close to the experimental ones they lay outside the error bars. A possible explanation of the discrepancy between experimental and estimated values can be that branching ratios could be energy-dependent (as it has been found in the present paper for the Cs $6s \leftarrow 7p$ transition and in other systems [27-29]). If the branching ratio energy dependence for the Cs $6s \leftarrow 6p$ is similar to that measured for Cs $6s \leftarrow 7p$, in the low collision energy range (as is the case in the present calculation), the cross-sections for $C_{s}(6p^{1/2}P_{3/2})$ reported in Fig. 9(a) would be overestimated, real

values being lower and consequently in better agreement with measured data.

Calculated total excitation cross-sections for $Cs(7p^{1} {}^{2}P_{1/2,3/2})$ are in average one order of magnitude larger than the measured emission crosssection values for decay to the ground atomic level $Cs(6s^{1} S_{1/2})$ as can be seen in Fig. 9(b). This was to be expected considering that $Cs(7p^{1} P_{1/2,3/2})$ can also decay to $Cs(7s^{1-2}S_{1/2})$ (and even from this to the Cs($6p^{1/2}P_{1/2,3/2}$)), the calculated excitation cross-section for $Cs(7p^{1/2}P_{1/2,3/2})$ being consequently overestimated. From the available information on the spectral lines for the Cs $7s \leftarrow 7p$ decay [47] and the total measured intensity in the laboratory for each transition, the total intensity for the Cs $7s \leftarrow 7p$ (not observed in our experiment) has been estimated [48], assuming similar values for the transition dipolar moments involved. Results thus obtained predict that the intensity of the non observed Cs $7s \leftarrow 7p$ transition should be about 0.9 times that for the Cs $6s \leftarrow 7p$ transition.

Using this result we have obtained the corrected excitation cross sections for $Cs(7p^{1-2}P_{1/2,3/2})$ from the original calculations and these values are also included in Fig. 9(b). It can be seen how the corrected excitation cross-sections lie not far now from the measured ones and are of the same order of magnitude. This improved agreement seems to point out that, although not measurable under our experimental conditions, the Cs $7s \leftarrow 7p$ decay plays an important role in diminishing the original population of the Cs $(7p^{1-2}P_{1/2,3/2})$ levels.

In the same way as target excitation cross-sections, hemiquantal calculations also allow to study charge transfer processes, in particular those leading to Na($3s^{1-2}P_{1/2,3/2}$) and to Na($4d^{1-2}D_{3/2,5/2}$) which have also been measured for the (CsNa)⁺ collision system. Calculated cross-section values for the first excited levels of Na are shown in Fig. 9(c), together with the experimental emission cross-section for Na($3s^{1-2}P_{1/2,3/2}$). There it can be seen how calculated values are lower than the experimental ones. Moreover the shape of the cross section vs. energy curves is not quite the same in the range of energies considered. The values for emission cross-section seem to point out that cascade effects from higher excited states do contrib-



Fig. 9. Experimental and computed emission cross-sections for the different observed exit channel in the $Cs(6 {}^{2}S_{1/2}) + Na^{+}({}^{1}S_{0})$ collision system as a function of the collision energy (E_{lab} and E_{CM}) (see text). (a) $Cs(6p^{1} {}^{2}P_{3/2})$ formation: (O) experimental, (\blacktriangle) calculated, (\blacklozenge) estimated; (b) $Cs(7p^{1} {}^{2}P_{1/2,3/2})$ formation: (O) experimental, (\blacklozenge) corrected; (c) $Na(3p^{1} {}^{2}P_{1/2,3/2})$ formation: (O) experimental, (\bigstar) calculated, (\bigstar) calculated $Na(3p^{1}) + Na(3d^{1})$; (d) $Na(4d^{1} {}^{2}D_{3/2,5/2})$ formation: (O) experimental, (\bigstar) calculated.

ute to Na(3s¹ ²P_{1/2,3/2}) population. In fact, experimental data reported in Fig. 4 have been corrected for the cascade effect from Na(4d¹ ²D_{3/2,5/2}) decay, but corrected values lie still within the error bars. On the other hand, decay from Na(3d ²D_{3/2,5/2}), which cannot be experimentally measured (its emission is at about 8194 Å, in a high-noise zone) could also be responsible for this discrepancy. If the lifetime of excited Na(3d¹) is shorter than that of Na(3p¹), then the true measured emission crosssection for Na(3p¹ ²P_{1/2,3/2}) would be lower, but the necessary correction of the experimental excitation function cannot be carried out for lack of data on the Na $3p \leftarrow 3d$ transition. However, assuming that Na(3d¹) lifetime is much shorter than that for Na(3p¹), then the emission cross-section from Na(3p¹ ${}^{2}P_{1/2,3/2}$) can be approximately evaluated by adding both calculated cross-sections leading to Na(3p¹) and to Na(3d¹). As can be appreciate in Fig. 9(c), hemiquantal emission cross-sections values calculated using this approximation are in quite good agreement with experimental data considering the experimental error in the range of energies calculated.

The last experimental emission cross-section measured in the $(CsNa)^+$ collision system is that of $Na(4d^{1 2}D_{3/2.5/2})$ produced by electron transfer. In this case, apart from the lack of experimental information, although the excited $Na(4f^1)$ can decay to $Na(4d^1)$, since the corresponding energy levels for both electronic configurations are almost degenerate, the 4d¹ configuration can be expected to have a very long lifetime, when compared with this decay, thus exerting a negligible influence on the population of levels associated with the 4d¹ configuration. In Fig. 9(d) calculated hemiquantal cross-sections are reported together with measured emission cross-section and it can be seen that agreement between both data sets is good enough considering the experimental error.

Dynamical calculations also permit to obtain the contribution of the radial $(\Sigma^+ - \Sigma^+)$ and angular $(\Sigma^+ - \Pi)$ non-adiabatic couplings to the total calculated cross-section values in the basis set of Σ^+ and Π states used. As the experimental entrance channel correlates with a molecular state of Σ^+ type, only the radial coupling contributes to crosssections for channels leading to Cs or Na atoms with a ns^1 electronic configuration, while rotational coupling can become important when other atomic electronic configurations like np^1 are possible. A case in point is the formation of $Cs(6p^{1} {}^{2}P)$ and $Cs(7p^{1} {}^{2}P)$, where both radial and angular coupling contributions to the total crosssection are 12.8% and 87.2% and 53.0% and 47.05%, respectively, at 425 eV in the CMF. For the electron transfer process leading to $Na(3p^{1} {}^{2}P)$ the radial contribution is 42.5% while the angular one is 57.5%. Both radial and angular couplings change with collision energy but the variation do not follow any particular trend.

Among the 18 asymptotic atomic electronic configurations for Cs and Na atoms included in the complete electronic wave function of the colliding system, for all collision energies studied the most favoured exit channel is $Na(3d^{12}D) + Cs^{+}$ whose cross-section values average about double than those for Na $(3p^{12}P)$ formation.

Other results obtained from hemiquantal dynamical calculations are total elastic cross-sections Table 2

Hemiquantal calculated cross-sections for the elastic $Cs(6s^{1\ 2}S)+Na^+$ and dark $Na(3s^{1\ 2}S)+Cs^+$ exit channels in collisions between Cs and Na^+ in their respective electronic ground states

$E_{\rm CMF}~({\rm eV})$	$\sigma(\mathrm{Cs}(6\mathrm{s}^{1-2}\mathrm{S}))$	$\sigma(\mathrm{Na}(3\mathrm{s}^{1-2}\mathrm{S}))$
425	2.90	0.30
600	3.10	0.20
770	3.60	0.17
850	4.30	0.16
1025	4.60	0.13
1195	4.30	0.12
1275	4.50	0.12

Cross-section values have to be multiplied by 10^{-14} and given in cm².

and cross-section for the electron transfer process leading to Na atom in the electronic ground state Na($3s^{1-2}S$) + Cs⁺ (the so-called "dark" channel) for which values are given in Table 2. Total elastic (Cs($6s^{1-2}S$) + Na⁺) cross-sections have the highest values by about one order of magnitude for all energies studied, which is in agreement with the predominance of elastic processes in elementary inelastic collisions. For the dark exit channel producing Na($3s^{1-2}S$) + Cs⁺, cross section values show an opposite energy dependence in comparison with other excitation or charge transfer processes measured and of the same order of magnitude in the range of energies considered.

6. Concluding remarks

Electronic excitation of Cs target atoms and charge transfer of impinging sodium atoms in the (CsNa)⁺ collision system in the energy range of 0.30–4.00 keV have been measured in crossed molecular beams experiments. Emission cross-section for Cs(6p¹ ²P_{3/2}), Cs(7p¹ ²P_{1/2,3/2}), Na(3p¹ ²P_{1/2,3/2}) and Na(4d¹ ²D_{3/2,5/2}) atomic levels have been obtained measuring fluorescence decay. In the case of Cs(7p¹ ²P_{1/2,3/2}) levels a non-statistical energy dependent cross section branching ratio for J = 3/2 and J = 1/2 has been measured, with the population of J = 3/2 level increasing at the highest energies values until it seems to tend to the statistical value. Cascade effects on the Na(3p¹ ²P_{1/2,3/2}) cross-sections from $Na(4d^{1} {}^{2}D_{3/2,5/2})$ decay have been considered, but their influence is negligible.

Hemiquantal dynamical calculations have been carried out for the (CsNa⁺) collisional system for energies below 1.60 keV in the LF. In order to describe non-adiabatic effects as well as possible the complete electronic wave function of the system has been expanded in a basis set of 18 $^{2}\Sigma^{+}$ and 12 $^{2}\Pi$ adiabatic states which include all experimentally detected exit channels. Hemiquantal calculations take into account both the radial and the angular non adiabatic couplings between all basis set electronic states and have been numerically obtained from ab initio pseudopotential calculations for the pseudomonoelectronic quasimolecule CsNa⁺.

Although in general a direct comparison of measured emission cross sections values with those obtained from hemiquantal calculations is not possible, after some corrective considerations, measured and calculated values are in relatively good agreement considering the experimental error, showing that hemiquantal dynamical calculations are able to provide an adequate description of the non adiabatic process considered.

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