Available online at www.sciencedirect.com
SCIENCE DIRECT®
Chemical Physics Letters 382 (2003) 106–111
CHEMICAL PHYSICS LETTERS
www.elsevier.com/locate/cplett

Electron capture processes in collisions between Mg ($6^2S_{1/2}$) atoms and $Na^+(^1S_0)$ ions in the 0.10–4.00 keV energy range

J. de Andrés, M. Sabidó, J.M. Lucas, J. Sogas, A. Aguilar *

Departament de Química Física, CeRQT/Parc científic de Barcelona, Universitat de Barcelona, C/Martí i Franquès, 1, 08028 Barcelona, Spain

Received 18 September 2003
Published online: 6 November 2003

Abstract

The fluorescence of excited species formed in collisions between neutral magnesium atoms and sodium ions has been studied experimentally using a crossed ion–atom beam technique. The only emission detected corresponded to the $Na(3^2P_{3/2,1/2}) \rightarrow Na(3^2S_{1/2})$ decay of neutral Na atoms formed by electron capture. Its strength has permitted to resolve it into its $J = 1/2$ and $J = 3/2$ states, and for the latter the M_j magnetic states have also been separated, cross-section dependence on collision energy or branching ratio being given for all of them.

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 ionized gases [1]. Relevant examples of ion-neutral processes are those taking place in interstellar clouds, planetary ionospheres, gas discharge and in plasma deposition of thin metal films. Ion–atom collisions are a current research topic in the field of Chemical Dynamics using molecular beams techniques, and among these the case where both atoms are alkali in nature has attracted much attention. This is due to a series of circumstances: both ion and neutral atom beams are relatively easy to generate, as is also the measure of the fluorescent emission from the decay of electronically excited atoms, but also because their main dynamical behavior can be studied performing relatively simple model calculations. In this field, since the pioneering experimental work on alkali ion–alkali atom systems done by Perel et al. ([2] and references cited there), interesting studied have been performed by Aquilanti et al. ([3] and references cited there), Tolk et al. [4], Andersen et al. [5], and Brunetti et al. [6], covering many symmetrical and asymmetrical alkali ion–atom pairs. More elaborated experiments involving alkali atoms excited by polarized lasers and devoted to observe the specific alignment effects on electron transfer collisions having been done by Bähring et al. [7] and more recently by Thomsen et al. [8].

* Corresponding author. Fax: +34-93-402-1231.
E-mail address: antonio@qf.ub.es (A. Aguilar).

0009-2614/$ - see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.cplett.2003.09.161

Taking into account the relatively simple electronic structure of the alkali atoms, where essentially only the single *n*s valence electron becomes excited in the energy range currently under study, worthwhile results on theoretical calculations can be obtained even using relatively simple models which take into account the intrinsic non-adiabatic nature of the electronic excitation or electron transfer processes. Thus, Aquilanti [9] improved earlier studies of Perel et al. [2] and Melius et al. [10], while McMillan [11] and Shingal et al. [12] performed semiclassical studies. Recently Nakamura et al. [13] 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 ([14] and references cited there) has been performed in the last decade by 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 ion–atom pairs allowing an interpretation of the most relevant experimental results obtained. Since information on collisions involving atoms with more than a single valence electron is rather scarce (see below), we have recently begun to employ alkali-earth targets, starting with magnesium atoms. In the range of relatively low collision energies (under 5.0 keV) in which we operate, only one of the two valence electrons of this atom can be expected to become excited, just as it happens on alkali–alkali collisions, but the presence of the second electron puts these systems into a higher complexity level, from the viewpoint of their theoretical interpretation at least. In particular, asymptotic excited channels can now correlate neutral Mg atoms in both singlet and/or triplet states, while charge transfer processes lead to the formation of fragments in doublet states. Thus, in principle, the system can evolve from the singlet entrance channel ($Mg(3s^2, {}^1S_0) + Na^+({}^1S_0)$ in this paper), correlating with a singlet quasimolecular state, and leads to the formation of asymptotic singlet, doublet or triplet atomic states through singlet and triplet quasimolecular states. Taking this fact into account, it can be expected that spin–orbit interaction will play an important role in the interpretation of experimental results. In this Letter we report on the first results, obtained for the $(Mg–Na)^+$ collisional system, which seems to offer the possibility of a direct application of the results obtained to the design or modification of light sources, for instance. This Letter is organized in the following way: 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 experimental results forms Section 4.

2. Experimental setup

A detailed description of the experimental crossed beam setup has been published already in [14]. In this apparatus a beam of alkali atoms (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 a right angle the thermal neutral beam of ground-state Mg atoms generated by heating in an oven. The fluorescence produced by decay of the excited electronic states produced in the collision is collected by an optical system placed perpendicularly to the collision plane over the scattering center, analyzed by a 50 cm monochromator and read by a photomultiplier. In order to optimize data collection, both signal intensity and ion current values are automatically scanned at 10 readings per second and stored in a multichannel system which furthermore ensures an optimal correlation between both sets of data.

Background pressure is usually maintained in the range of 10^{-7}–10^{-6} mbar during experiments. In order to report absolute cross-section values, experiments on the $Mg + e^-$ system were done to calibrate our experimental system [15]. To this end cross-sections for the inelastic process $Mg({}^1S_0) + e^- \rightarrow Mg(3^1P) + e^-$ were measured in arbitrary units and then compared with previously reported data [16] in absolute units, normalizing

them at 1400 eV collision energy in the laboratory frame of reference.

3. Experimental results

3.1. Total cross-sections

In the collision between Mg and Na^+ no wavelengths attributable to direct magnesium excitation were observed in the whole energy range studied, and among the possible neutral sodium emissions only the one corresponding to the decay of the first excited state formed by electron transfer from Mg could be measured:

$$Mg(3^1S) + Na^+(^1S_0) \rightarrow Na(3^2P_{1/2,3/2}) + Mg^+(^1S_0)$$

$$Na(3^2P_{1/2,3/2}) \rightarrow Na(3^2S_{1/2}) \quad \lambda = 5889\text{–}5895A$$

For this transition, total excitation cross-section dependence on collision energy is given in Fig. 1. Such a result seems somewhat unusual since for this transition signal strength is high enough (experimental threshold is well below 500 eV in the laboratory frame of reference) that, at least in alkali–alkali collisions other, higher energy transitions ought to be observed too, but by comparing these results with some preliminary ones obtained for Mg–Rb^+ and Mg–Cs^+ it is possible to see that there is a tendency in Mg–X^+ collisions for electron transfer processes to become more efficient when ion mass increases. On the other hand, while there are not many experimental data about ion–atom inelastic collisions involving closed-shell alkali-earth targets atoms: Aquilanti et al. report on inelastic collisions in Hg–Na^+ [20,21] and Cd–Na^+ [22] system. However, taking into account the different electronic structure nature of the closed shell Hg and Cd target atoms, different behavior can be expected when comparing with those obtained for the Mg–Na+ system. Thus, in the same energy range we have studied, the Hg + Na^+ collision leads to the excitation of mercury to both $Hg(6^3P_1)$ and $Hg(6^3D_{1,2})$, and the electron capture channel leading to $Na(3^2P)$ was also measurable. In the case of Cd–Na^+ system only the direct excitation channels leading to $Cd(^1P_1)$ and $Cd(^3P_1)$ could be measured.

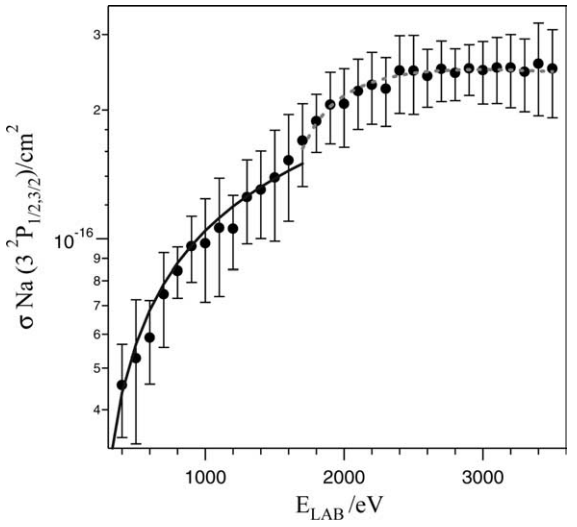

Fig. 1. Total emission cross-section vs. collision energy (in the laboratory frame of reference) for the $Na(3^2P_{1/2,3/2}) \rightarrow Na(3^2S_{1/2})$ decay in Mg–Na+ collisions. Full line represents fitting by a LZS rotationally coupled model, dotted line the same by radially coupled one.

It is also worth noting in Fig. 1 that excitation function shape differs considerably from equivalent ones in alkali–alkali collisions [14], lacking a maximum and having instead a noticeable inflection at some 1700 eV collision energy and leveling out at some 2600 eV, both energies in the laboratory frame of reference. When comparing it with the equivalent one for Hg–Na^+ it can be appreciated how the shape is rather similar. Moreover, both dependences tend to level out at high energies at similar cross-section values (some 4.5×10^{-16} cm^2 for $(Hg–Na)^+$ [21] and about 2.5×10^{-16} cm^2 for $(Mg–Na)^+$).

3.2. State-to-state cross-sections for the $Na(3^2P_{1/2\,,\,3/2}) \rightarrow Na(3^2S_{1/2})$ decay

For this transition, the relatively strong signal obtained has permitted to increase the resolution to allow separation of the two $J = 1/2$ and $J = 3/2$ states and thus the study of their relative population dependence on collision energy, the corresponding branching ratio being shown in Fig. 2. It can be readily appreciated how in the energy range studied all values lie below the statistical value of two, meaning that the $J = 1/2$ state is relatively

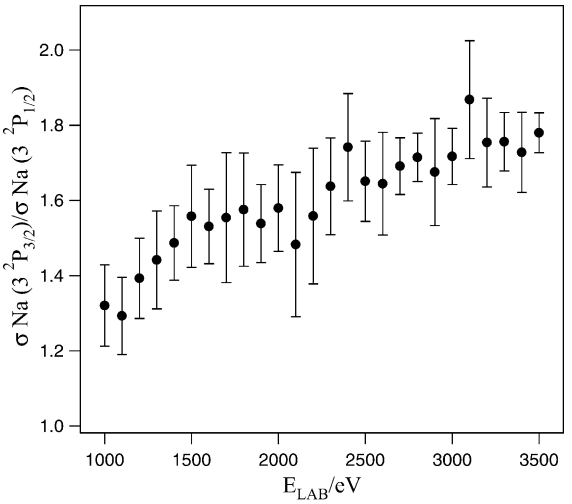

Fig. 2. Branching ratio $\sigma(Na(3^2P_{3/2}))/\sigma(Na(3^2P_{1/2})$ vs. collision energy (in the laboratory frame of reference) for the $Na(3^2P_{1/2,3/2}) \rightarrow Na(3^2S_{1/2})$ decay in Mg–Na^+ collisions.

more populated than was to be expected according to a statistical behavior. There is a marked energy dependence (the most directly comparable alkali–alkali collision in terms of mass, Na + Na^+, shows a negligible dependence for the same spectral line [14]) and signs of an oscillatory structure which, however, is far too small when compared to error bars to be interpreted.

3.3. Polarization of the $Na(3^2P_{3/2}) \rightarrow Na(3^2S_{1/2})$ fluorescent emission

When a linear polarizing filter was installed in the system's light path, a marked polarization effect was observed for this spectral line, which can only arise from the non-statistical population of its magnetic sublevels. However, a lesser effect was also observed for the $Na(3^2P_{1/2}) \rightarrow Na(3^2S_{1/2})$ decay which, being of the 1/2–1/2 type, should not to show any polarization at all [14], but this can be justified considering that many components of the optical systems (monochromator, lenses and others) may act as polarizers distorting the fluorescent emission. This effect was exploited to quantify this distortion, using this information to correct the $Na(3^2P_{3/2}) \rightarrow Na(3^2S_{1/2})$ data and to obtain its true polarization fraction values (as usually defined [17]) as well as their energy dependence, which is shown in Table 1. It can be seen that there is a marked negative dependence on collision energy and that the fraction inverts at some 2400 eV.

When measuring de-excitation cross-sections, these must be corrected for possible anisotropic effects in order to obtain the true excitation cross-section. This can be done by means of the polarization fraction [17] and such corrected values are represented along with the originals in Fig. 3. The very low strength intensity measured when the polarizer is in place made it impossible to measure polarization fractions at the lower collision energy values, where it can be readily appreciated that, for all points for which both values could be determined, divergence between corrected and original data is negligible.

Polarization measurements contain also information about magnetic sublevel population, and it is possible to obtain magnetic cross-section values by using angular momenta algebra (see [18] for

Table 1
Polarization fractions as a function of collision energy for the $Na(3^2P_{3/2}) \rightarrow Na(3^2S_{1/2})$ decay in Mg–Na^+ collisions

E (eV)	Polarization fraction	E (eV)	Polarization fraction	E (eV)	Polarization fraction
1000	−0.24	1900	0.10	2800	0.05
1100	−0.23	2000	−0.10	2900	0.10
1200	−0.07	2100	0.01	3000	0.12
1300	−0.29	2200	0.02	3100	0.09
1400	0.05	2300	0.00	3200	0.11
1500	0.07	2400	0.09	3300	0.11
1600	−0.08	2500	0.01	3400	0.14
1700	0.05	2600	0.04	3500	0.16
1800	0.10	2700	−0.02		

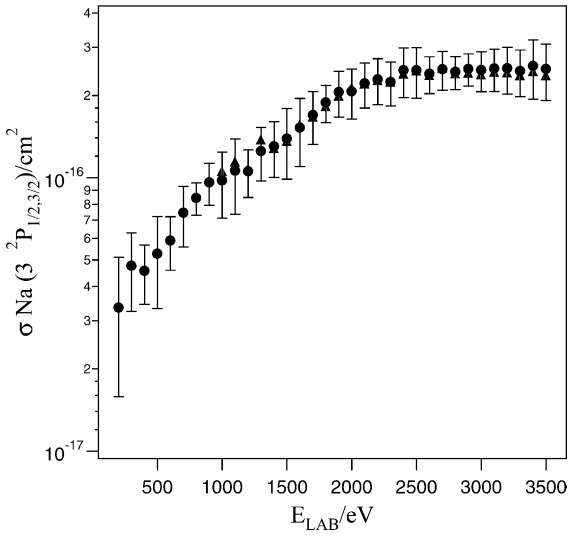

Fig. 3. Emission (circles) and excitation (triangles) cross-sections as a function of collision energy.

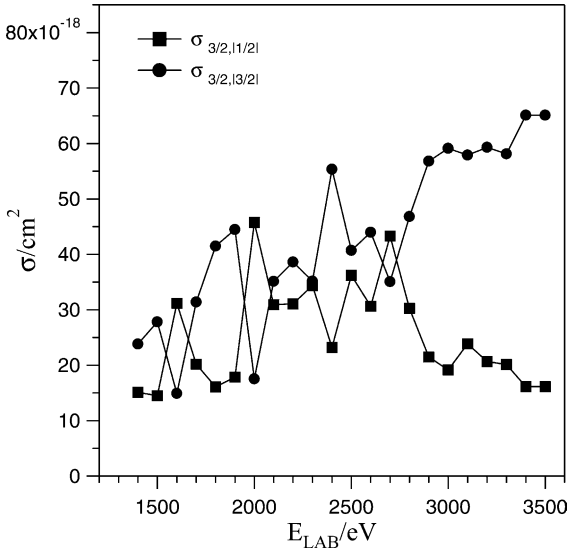

Fig. 4. Magnetic cross-sections dependence on collision energy for $Na(3^2P_{3/2})$ formation in Mg–Na^+ collisions.

details). Magnetic cross-sections for both absolute values of the M_j components ($|M_j|$) are represented in Fig. 4. It is interesting that, like similar processes in Rb–Rb^+, Rb–Na^+ and Na–Rb^+ collisions, their energy dependence is positive and that population of the $|M_j| = 3/2$ state is favoured at higher collision energies. Unfortunately, a comparison with the corresponding one for the charge transfer processes in Hg–Na^+ and Cd–Na^+ [20–22] is not possible because authors report only on the magnetic cross-sections energy dependence for neutral target excitations.

4. Discussion

A first approximation to an interpretation of the experimental results can be obtained by applying to them a simple two-state model such as that of Landau–Zener–Stuckelberg (LZS) [14] even when, as is the case here, collision processes involve a manifold of states which correlate with different excited channel products. In Fig. 1 are represented the results of such a fitting: It can be readily appreciated that, at low energies, a rotationally coupled LZS model [9] manages to fit quite well the experimental results. This could mean that the process is essentially controlled by a Σ–Π type coupling, the calculated threshold energy of 137.7 eV lying far outside the range of the experimental setup. The proportionality constant 4.12×10^{-18} $eV^{-1/2}\,cm^2$ is of the same order of magnitude as those observed in alkali–alkali collisions in which this spectral line is also observed [14].

At the unusually low energy of 1700 eV in the laboratory frame (when compared with alkali–alkali collisions) the fitting becomes invalid and it is necessary to use a LZS radially coupled model in order to obtain a good fit for the remaining experimental data. Moreover, the transition zone coincides with the minimum already mentioned, although calculated threshold energy has a much lower value of only 1492.5 eV, while the proportionality constant has a value of 1.92×10^{-14} $eV^{-1/2}\,cm^2$, well within usual alkali–alkali values for this process. The presence of both kinds of coupling in the energy range considered may mean either that the electron capture process involves essentially both Σ–Σ coupling and a Σ–Π one, or that the global behavior of this system is such that a simple two-state model is unable to describe it properly. Therefore it may be necessary to take into account the full manifold of states involved

and the corresponding couplings between them in order to get a meaningful interpretation of the experimental results.

To the best of our knowledge the most elaborated theoretical study on the $(Mg–Na)^+$ system [19], reports on the potential energy curves for five of six low-lying asymptotic states at different levels of ab initio calculations as well as the radial and rotational couplings between some of them. According to such results, we should have been able to observe fluorescent emissions from excited magnesium atoms in our experiments, but as it has been already said, this was not the case. It seems, therefore that more theoretical effort needs to be devoted to the study of the ion–atom systems involving more than one valence electron, including dynamical calculations. This is especially true in the case of the $(Mg–Na)^+$ system, for which high-quality ab initio calculations and dynamical studies are being developed by our research group.

Acknowledgements

This work has been supported by the Spanish DGICYT project PB97-0919, the Spanish Ministry of Science and Technology project BQU2001-3018 and the Generalitat de Catalunya-DURSI project 2000SGR 00016. M.S. thanks to the Universitat de Barcelona for a research grant. J. de A. wishes to thank also the personnel of Optica Cottet for their help in solving a technical problem.

References

[1] D.L. Lambert, Phys. Scr. T47 (1993) 186.
[2] H. Daley, J. Perel, Phys. Rev. A 4 (1971) 162.
[3] V. Aquilanti, P. Casavecchia, G. Grossi, J. Chem. Phys. 71 (1979) 3547.
[4] N.H. Tolk, C.W. White, S.H. Neff, W. Lichten, Phys. Rev. Lett. 11 (1973) 671.
[5] J.Ø. Olsen, N. Andersen, T. Andersen, J. Phys. B 10 (1977) 1723.
[6] B. Brunetti, F. Elisei, C. Vergari, Nuovo Cimento 63 (1981) 98.
[7] A. Bhäring, I.V. Hertel, E. Meyer, H. Schmidt, Phys. Rev. Lett. 53 (1984) 1433.
[8] W. Thomsen, N. Andersen, E.E.B. Campbell, I.V. Hertel, S.E. Nielsen, J. Phys. B: At. Mol. Opt. Phys. 31 (1998) 3429.
[9] V. Aquilanti, Z. Physik. Chem. 90 (1974) 1.
[10] C.F. Melius, W.A. Goddard III, Phys. Rev. Lett. 29 (1972) 975.
[11] W.L. McMillan, Phys. Rev. A 4 (1971) 69.
[12] R. Shingal, J.C. Noble, B.H. Brandsen, D.R. Flower, J. Phys. B 19 (1986) 3951.
[13] H. Nakamura, C. Zhu, J. Chem. Phys. 101 (1994) 10630.
[14] J. Sogas, M.E. Aricha, J. de Andrs, M. Albert, J.M. Lucas, A. Aguilar, Phys. Chem. Chem. Phys. 3 (2001) 3638.
[15] A. Salichs, Master Thesis, Universitat de Barcelona, 2000.
[16] D. Leep, A. Gallagher, Phys. Rev. A 13 (1976) 751.
[17] N. Bendali, D.H. Duong, P. Juncar, J.M.St. Jalm, J.L. Vialle, J. Phys. B 19 (1986) 233.
[18] S.T. Chen, A.C. Gallagher, Phys. Rev. A 17 (1978) 571.
[19] J.P. Bruna, S.D. Peyerimhoff, in: I. Prigogine, S.A. Rice (Eds.), Advances in Chemical Physics, vol. LXVII, John Wiley & Sons, Chichester, 1987, p. 1.
[20] V. Aquilanti, P. Casavecchia, Chem. Phys. Lett. 47 (1977) 288.
[21] V. Aquilanti, P. Casavecchia, G. Grossi, J. Chem. Phys. 68 (1978) 1499.
[22] V. Aquilanti, P. Casavecchia, G. Grossi, J. Chem. Phys. 71 (1979) 3546.