

# The $\Pi_{1/2} - \Pi_{3/2}$ Rb and Cs desorption conundrum

M. Barranco<sup>\*1</sup>, F. Coppens<sup>‡</sup>, N. Halberstadt<sup>‡</sup>, A. Leal<sup>\*</sup>, M. Mudrich<sup>†</sup>, M. Pi<sup>\*</sup>, F. Stienkemeier<sup>†</sup> and J. von Vangerow<sup>†</sup>

<sup>\*</sup> Departament FQA and IN<sup>2</sup>UB. Facultat de Física, Universitat de Barcelona. Av. Diagonal 645, 08028 Barcelona, Spain

<sup>‡</sup> LCAR, IRSAMC, UMR 5589, CNRS et Université Paul Sabatier-Toulouse 3, F-31062 Toulouse Cedex 09, France

<sup>†</sup>Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg, Germany

**Synopsis** The desorption of Rb and Cs atoms photo-excited from the ground ns state to the excited np states has been simulated within TDDFT. Arguments are presented indicating that relaxation from the  $^2\Pi_{3/2}$  to the  $^2\Pi_{1/2}$  excited state makes the simulations compatible with experiments. It also provides a simple explanation for some of the experimental findings on the sinking of Rb<sup>+</sup> and Cs<sup>+</sup> cations produced by photo-ionization of the photo-excited alkali atom.

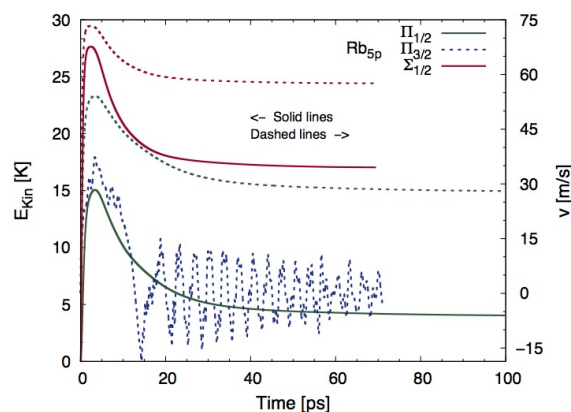
The real-time dynamics of photo-excited Rb atoms has been studied using femtosecond imaging spectroscopy and time-dependent density functional theory (TDDFT) [1]. A similar study is being conducted for Cs atoms; details on the TDDFT approach can be found in [2] and references therein.

Figure 1 shows the velocity and kinetic energy of the Rb atom excited to the 5p state as a function of time. Similar results have been found for Cs, the velocities being smaller for this alkali. One may conclude that within TDDFT: a) Rb excited to the  $5p^2\Sigma_{1/2}$  state is detached. This is in agreement with experiments. b) Rb excited to the  $5p^2\Pi_{1/2}$  state is detached. This is not in conflict with experiments showing that Rb excited to the low energy region of the D1 line remains attached to the droplet [3], as our simulations are for the peak energy. c) Rb excited to the  $5p^2\Pi_{3/2}$  state is not detached; it builds an exciplex in about 10 ps that remains on the droplet surface. This is in apparent contradiction with the experiments that show its ejection [4].

How can the simulations be reconciled with the experimental findings of [3, 4]? One has to distinguish the state to which the Ak is experimentally excited, that is fairly well determined by the chosen excitation energy, from the state in which the Ak atom is being detected. Usually, this state is not determined in the experiments.

We argue that the  $5p^2\Pi_{3/2}$  exciplex is not detached as such. Rather, it first de-excites non-radiatively to the  $5p^2\Pi_{1/2}$  state that may be ejected either as bare Rb\* or as exciplex. The de-excitation does not take Rb\* necessarily to the low energy region of the D1 line; therefore, there is no reason why it should remain on the droplet surface. Moreover, Rb  $5p^2\Pi_{1/2}$  keeps part of the de-excitation energy as kinetic energy that helps it to be ejected.

This explains two key experimental findings, namely that Rb excited to the D2 line (nominally the  $5p^2\Pi_{3/2}$  state): a) May indeed be detached, but not from the originally excited state; rather, from the  $5p^2\Pi_{1/2}$  state to which it has previously relaxed. b) When photo-ionized, it does not lead to the sinking of Rb<sup>+</sup>, as the ejected Rb\* is photo-ionized away from the droplet. We will show that this also explains the experimental findings on the sinking of Cs<sup>+</sup> similarly produced by photo-ionization of 6p Cs\*.



**Figure 1.** Velocity (dashed lines, right scale) and kinetic energy (solid line, left scale) of the Rb atom excited to the the 5p state. The kinetic energy of the  $^2\Pi_{3/2}$  state is not given as this state is not ejected.

## References

- [1] J. von Vangerow *et al.* 2017 *J. Phys. Chem. Lett.* **8**, 307.
- [2] A. Leal *et al.* 2016 *J. Chem. Phys.* **144**, 094302.
- [3] G. Auböck *et al.* 2008 *Phys. Rev. Lett.* **101**, 035301.
- [4] M. Theisen *et al.* 2011 *J. Chem. Phys.* **135**, 074306.

<sup>1</sup>E-mail: [manuel@fqa.ub.edu](mailto:manuel@fqa.ub.edu)