Real time excited state dynamics of alkali-doped helium nanodroplets: A TDDFT study

Maxime Martinez[*], François Coppens[*], Manuel Barranco[*†‡], Nadine Halberstadt[*][1], Martí Pi[†‡],

[*] Laboratoire des Collisions, Agrégats, Réactivité , IRSAMC, UMR 5589, CNRS et Université Paul Sabatier-Toulouse 3, 118 route de Narbonne, F-31062 Toulouse Cedex 09, France

[†] Departament FQA, Facultat de Física, Universitat de Barcelona. Diagonal 645, 08028 Barcelona, Spain

[†] Institute of Nanoscience and Nanotechnology (IN2UB), Universitat de Barcelona

Synopsis The real-time dynamics of excited alkali metal atoms (K, Rb, Cs) attached to quantum fluid He nanodroplets is investigated using time-dependent density functional theory (TDDFT), and comparing with available experimental results.

We report a theoretical investigation of the excited state dynamics of alkali-doped He nanodroplets in real-time. He nanodroplets are intriguing, quantum fluid objects of finite size. Doping them with alkali atoms makes them a particularly interesting model to study the fate of an excited atomic or molecular system in or on them. Alkali atoms are known to sit in a dimple at the droplet surface [2, 3], and to usually desorb upon electronic excitation, except for Rb [4] and Cs [5] excited close to the gas phase D1 transition. In addition, the alkali atom can bring along one or a few helium atoms and desorb as an exciplex. During the past few years, several real time dynamics experiments have been conducted on superfluid helium nanodroplets doped with alkali atoms using femtosecond pump-probe laser techniques [6]. In particular, the combination of fs pump-probe spectroscopy with velocity map imaging has allowed to clearly disentangle complex formation, desorption, and ion solvation.

Helium density functional theory (He-DFT) approach and its time-dependent version (He-TDDFT) are the best compromise between accuracy and feasibility to study the stability and real time dynamics of doped helium droplets with a size comparable to experiments.[7, 8]. We have used He-DFT and He-TDDFT [9] to model the photodissociation dynamics of Rb and Cs, for which fs pump-probe spectroscopy combined with velocity map imaging experiments have been conducted [10]. The results of the simulation can therefore be directly compared with experiments. For Rb excited to 5p and 6p, desorption occurs on strikingly different time scales ($\sim$100 *vs* $\sim$1 ps, respectively). The comparison between theory and experiment indicates that desorption proceeds impulsively for 6p excitation, whereas it is intermediate between impulsive dissociation and complex desorption for 5p excitation [10].

We have also applied He-DFT and He-TDDFT to study the photodissociation of potassium atoms from helium droplets. The desorption lifetimes obtained experimentally appear to be contradictory [11, 12]. In addition, potassium is very interesting limiting case between classical and quantum behavior. We will show results for K(4p) excitation in an attempt to solve the controversy, and for (5s) excitation in order to explore quantum effects in the desorption.

[1] E-mail: maxime.martinez@irsamc.ups-tlse.fr

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