Dynamics of photo-excited Ba^+ cations in helium nanodroplets

A. Leal,[1] M.Barranco,[1] F. Cargnoni,[2] M. Drabbels,[3] A. Hernando,[4] D. Mateo,[1] M. Mella,[5] M. Pi[1]

[1]Departament E.C.M., Facultat de Física, and IN^{2}UB, Universitat de Barcelona, Diagonal 645, E-08028 Barcelona, Spain
[2]Instituto di Scienze e Tecnologie Molecolari (ISTM), Consiglio Nazionale delle Ricerche, via Golgi 19, 20133 Milano, Italy
[3]Laboratoire de Chimie Physique Moleculaire, Swiss Federal Institute of Lausanne (EPFL), CH-1015 Lausanne, Switzerland
[4]Laboratory of Theoretical Physical Chemistry, Institut des Sciences et Ingenierie Chimiques, Swiss Federal Institute of Technology Lausanne (EPFL), CH-1015 Lausanne, Switzerland
[5]Dipartimento di Scienza ed Alta Tecnologia, Universita degli Studi dell'Insubria, via Valleggio 11, 22100 Como, Italy

Abstract

Within TDDFT, we have addressed the dynamics of Ba^+ cations in helium nanodroplets. The absorption spectra from S to P and D states, as well as the emission spectra from P to S and D states of the cation are discussed. The appearance of exciplexes is discussed and the dynamics of the excited Ba^+ cation in the P state has been investigated.

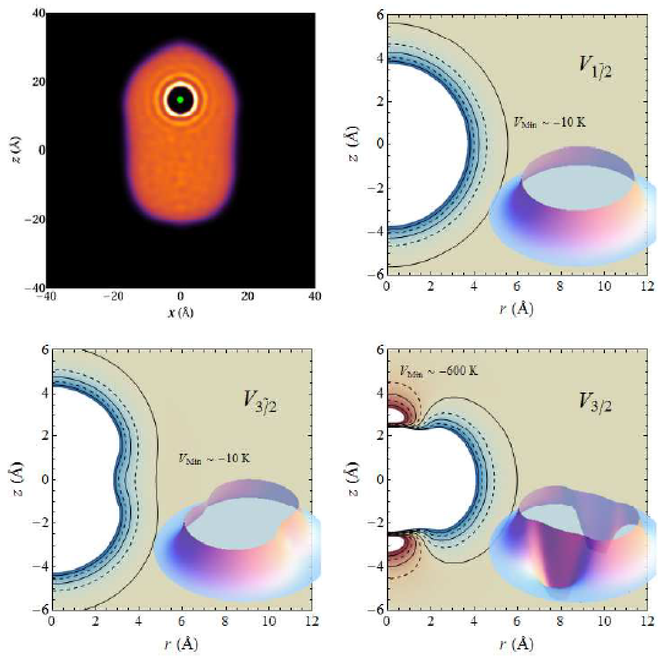
Potentials

For the ^{2}P states, the pair potentials have been written as a direction-dependent combination of Π and Σ potentials

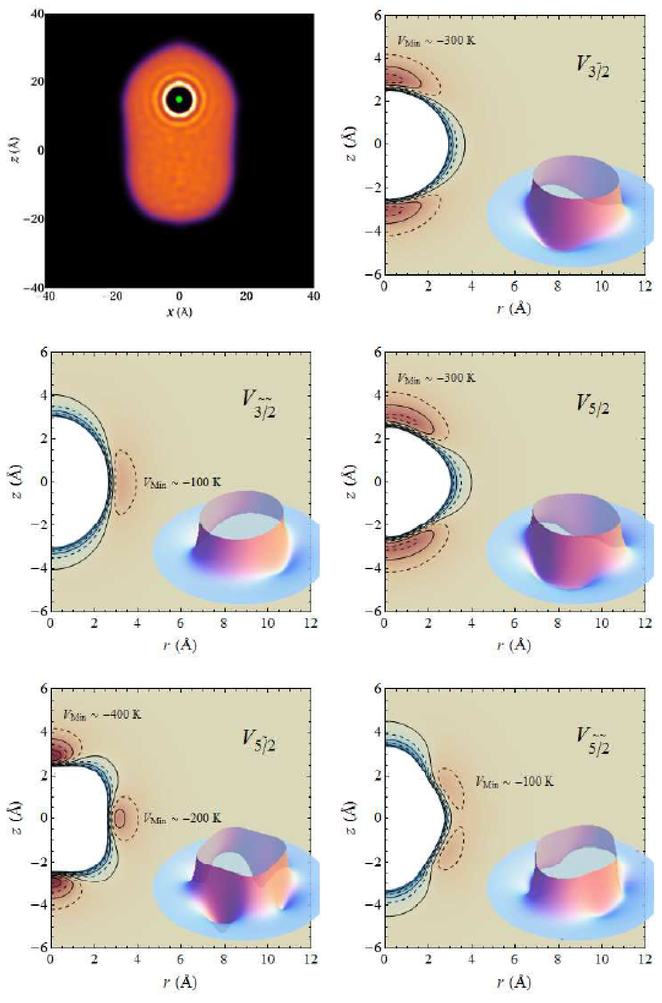
$$V_\lambda(\mathbf{r}) = \langle\lambda|V(r)|\lambda\rangle = \sum_{ijss'} \lambda^*_{is}\mathcal{V}^{ijss'}(\mathbf{r})\lambda_{js'},$$

where the six-dimentional matrix operator V has components

$$\mathcal{V}^{ijss'}(\mathbf{r}) = \left[V_\Pi(r)\delta_{ij} + (V_\Sigma(r) - V_\Pi(r))\,\frac{r_i r_j}{r^2}\right]\delta_{ss'}.$$



Using a generalization of the method above, the corresponding potentials for the ^{2}D states can be obtained



For both cases, the density used to calculate the potentials is the one showed in the top-left panel of each figure, corresponding to a turning point of the neutral Ba^+ dynamics.

References

[1] D. Mateo et al., PCCP **15**, 18388-18400 (2013)

[2] D. Mateo et al., J. Chem. Phys. **140**, 131101 (2014)

[3] H.J. Reyher et al. Phys. Lett. A **115**, 238 (1986).

DFT Framework [1]

The dynamic evolution of the electronic excited state of Ba^+ is described introducing an additional degree of freedom, a six-component vector $|\lambda\rangle$ written in terms of same basis for spin and angular momentum used for the SO interaction.

$$|\lambda\rangle = \sum_{is} \lambda_{is}(i,s)$$

The total energy of the $Ba^+@^4He_{1000}$ complex suddenly excited to the ^{2}P manifold is written as

$$E[\Psi, r_{Ba^+}, \lambda] = \int dr \frac{\hbar^2}{2m_{He}}|\nabla\Psi|^2 + \frac{p^2_{Ba^+}}{2m_{Ba^+}} + \int dr\varepsilon_{He}[\rho] + \langle\lambda|V_{SO}|\lambda\rangle + \int dr\rho(r)V_\lambda(r - r_{Ba^+})$$

The following coupled 3D time-dependent system, resulting from the variation of the action, has to be solved to obtain the dynamical evolution

$$i\hbar\frac{\partial}{\partial t}\Psi_{He} = \left[-\frac{\hbar^2}{2m_{He}}\nabla^2 + \frac{\delta\varepsilon_{He}}{\delta\rho(r)} + V_\lambda(r - r_{Ba^+})\right]\Psi_{He} \qquad , \qquad i\hbar\frac{\partial}{\partial t}|\lambda\rangle = \mathcal{H}|\lambda\rangle$$

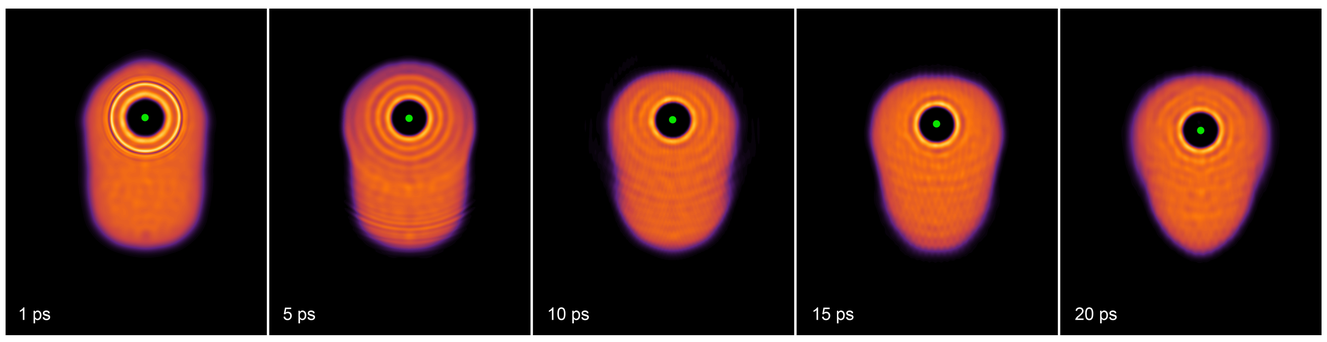
$$m_{Ba^+}\ddot{r}_{Ba^+} = -\nabla_{r_{Ba^+}}\left[\int dr\rho(r)V_\lambda(r - r_{Ba^+})\right] = -\int dr\nabla\rho(r)V_\lambda(r - r_{Ba^+})$$

The electronic state Hamiltonian $\mathcal{H}$ is a 6×6 matrix whose elements are given by

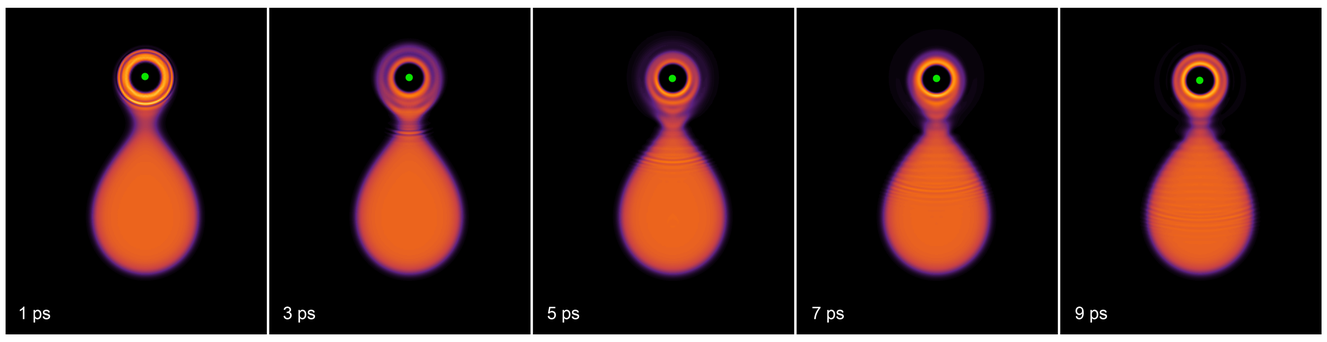
$$H^{ijss'} = \int dr\rho(r)\mathcal{V}^{ijss'}\left(r - r_{Ba^+_0}\right) + V^{ijss'}_{SO}$$

$^2P_{1/2}$ Dynamics

To solve the above equations initial values for the variables are required. We have chosen as starting configuration that corresponding to the turning point reached by the Ba^+ in the ground state 223 ps after the ionization of neutral Ba in the surface dimple state.[2]

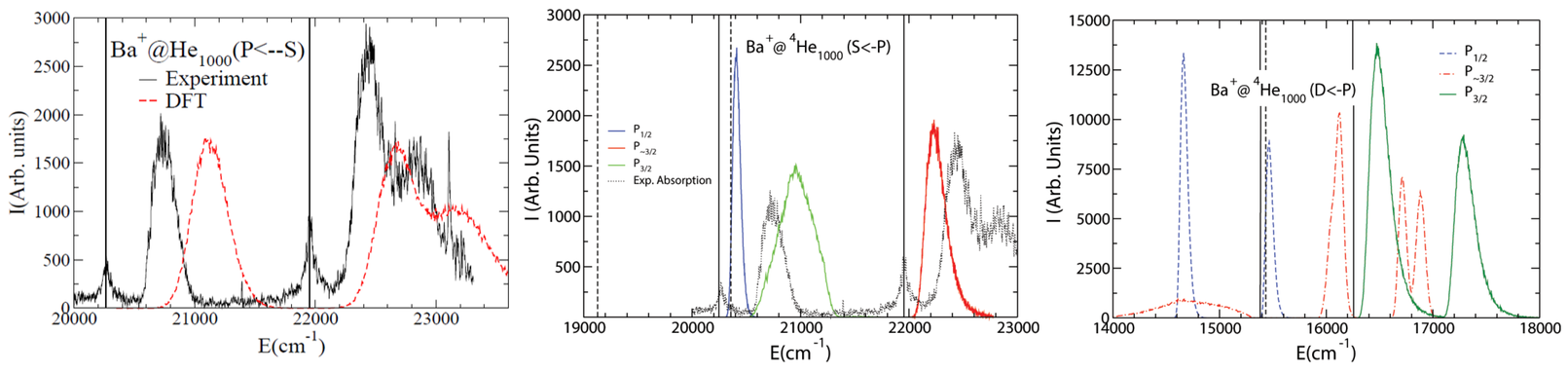


We have also followed the dynamic evolution of some particular configurations, like a metastable stretched configuration corresponding to $z_0 = 44.6$Å.



Absorption spectrum and preliminary results on emission spectra

We have calculated the absorption and emission spectra of Ba^+ between the ground state and ^{2}P and ^{2}D manifolds. The absorption spectrum and some preliminary results on the emission spectra are shown in the figure below.



In the absorption spectrum (left panel) the dashed line corresponds to the calculated spectrum while the solid one shows the experimental results. The center panel shows the S ⟵ P emission spectrum, where the coloured solid lines represents the emission lines and in order to compare, the dotted one shows the experimental absorption spectrum. The D ⟵ P emission spectrum is shown in the right panel. In the three panels, the vertical solid lines represent the persistent lines of singly ionized barium in the gas phase and the vertical dashed lines indicate the experimental peaks found in this energy region.[3]