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Scientific report

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Purpose of the visit

The main purpose of the visit was to complete developing and implementing the mean-field dynamics method with quenching the electronic wave function outside the non-adiabatic coupling region applied to rare-gas cluster cations, testing its functionality, and performing first, preliminary calculations on post-ionization fragmentation of rare-gas clusters. A detailed knowledge of the post-ionization fragmentation processes is crucial for a proper interpretation of experimental data obtained for clusters ionized via electron (or photon) impact. A powerful tool for the theoretical treatment of these processes in rare-gas cluster cations has proved hemiquantal dynamics, based on the Eherenfest mean-field approach combined with a semiempirical method (*diatomics-in-molecules*) for modelling the intra-cluster interactions [A. Bastida et al., CPL 249 (1996) 1]. The mean-field approach frequently yields to unphysically mixed quantum states, however, which makes difficult to interpret some of the computational data properly. A possible solution of this problem consists in introducing decoherence processes into the calculation after the fragmenting system has left the region of strong non-adiabatic couplings [M. D. Hack and D. G. Truhlar, JCP 114 (2001) 9305]. A simple way how to model the decoherence processes is a quenching of the electronic wave function (a jump from current electronic state to a properly selected, e.g. most probable, adiabatic state) – a method investigated during the present short visit stay.

Work carried out

Our previously developed programs for simulating non-adiabatic processes in rare-gas cluster cations using the Ehrenfest mean-field dynamics have been augmented with a code implementing decoherence jumps (quenching of the electronic wave function and adjusting nuclear velocities). Preliminary tests of the newly developed code (i. e., different quenching methods) have been performed for the post-ionization fragmentation of argon and xenon trimers, and for photodissociation of argon and xenon trimer cations; the results have been compared with previously published data obtained within pure mean-field approach [D. Hrivňák et al. Europhys. Lett. 71 (2005) 42 and I. Janeček et al. JCP 125 (2006) Art.No. 104315]. Additional calculations have been launched to test the efficiency of the internal conversion of the initial electronic excitation during the photodissociation of larger argon cluster cations (for Ar_5^+ in particular, which can be directly compared to available experimental data). Further programming work has been started to implement a benchmark "natural decay of mixing" method due to Truhlar and coworkers [M. D. Hack and D. G. Truhlar, JCP 114 (2001) 9305].

Main results

The main results of the work done during this short visit are a) a new set of augmented programs for simulating non-adiabatic processes in the rare-gas cluster cations (including the highly important case of the post-ionization fragmentation) and b) tests of the newly developed code carried out by comparing present computational data with either earlier calculations or available experimental results.

Future collaboration

The present project represents part of a broader aim shared by the Ostrava and Toulouse groups focusing on non-adiabatic processes in ionized rare-gas clusters. In the nearest future, the newly developed programs will be used in extensive calculations of post-ionization fragmentation (and also photodissociation) of larger rare-gas clusters. The program modules are quite general and are planned to be further used in simulations of (reactive) collisions of ionic and neutral rare-gas clusters.

Projected publications

The present study visit has promoted or even initiated several directions of prospective research in the field of the non-adiabatic dynamics of rare-gas cluster cations. In particular, there are several publications planned for the future concerning post-ionization fragmentation (and photodissociation) dynamics in these species. In addition, a publication is currently being prepared for submitting to the Journal of Chemical Physics, coauthored by D. Hrivnak, R. Kalus (both Ostrava), and F. X. Gadea, focusing on the dynamics of fragmentation of argon, krypton, and xenon trimer cations following absorption of a photon.