UV-pump/UV-probe spectroscopy of N_2

UV-pump/UV-probe spectroscopy of N_2

V J Borràs[1], J González-Vázquez[1], M Klinker[1] and F Martín[1,2,3]

[1]Departamento de Química, Módulo 13, Universidad Autónoma de Madrid, 28049 Madrid, Spain
[2]Instituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA-Nano), Campus de Cantoblanco, 28049 Madrid, Spain
[3]Condensed Matter Physics Center (IFIMAC), Universidad Autónoma de Madrid, 28049 Madrid, Spain

Synopsis UV-pump / UV-probe photoelectron spectra of N_2 are theoretically evaluated by solving the time-dependent Schrödinger equation in a basis of all-electron bound and continuum eigenstates provided by the XChem code.

The theoretical description of molecular photoelectron spectra in UV-pump/UV-probe experiments requires a good representation of the system's ionization continuum. For polyelectronic molecules, however, this is still a challenge due to the complicated short-range structure of correlated electronic wave functions. Whereas Quantum Chemistry Packages (QCP), implementing sophisticated methods to compute bound electronic molecular states, are nowadays standard in most laboratories, comparable tools for the continuum are not yet widely available. To tackle this problem a new approach developed in our group that uses a hybrid Guassian-B-spline (GABS) basis [1] (see Fig. 1), interfaced with existing QCPs via close-coupling scattering methods [2], has been used for the study of the multichannel ionization of molecular nitrogen.

In our group, single-photon ionization of N_2 has already been described within the fixed-nuclei approximation [3], and two-photon ionization of N_2 by assuming that the photons are absorbed sequentially [4], which are valid approximations when the pump and probe pulses are very short and do not overlap in time, respectively. The present study goes a step farther and includes a proper nuclear dynamics propagation as well as the possibility to describe absorption of more than one photon simultaneously. More specifically, we have solved the Time Dependent Schrödinger Equation (TDSE) in a basis of bound and continuum molecular states obtained from the XChem approach. To better handle the multichannel character of the ionization process while the nuclei move, we have developed a special methodology based on the projection of the XCHEM electronic states into the different parent ions and excited states of the neutral molecule. The calculated UV-pump / UV-probe photoelectron spectra show that the signature of nuclear dynamics is imprinted in the phases of the interferences observed in the temporal region where the pump and the probe pulses overlap.

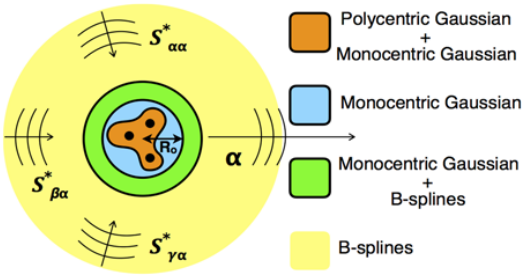

Figure 1. Schematic representation of the GABs basis.

References

[1] Marante C *et al* 2014 *Phys. Rev. A* **90** 012506
[2] Marante C *et al* 2017 *J. Chem. Theory Comput.* **13** 499
[3] Klinker M *et al* 2018 *J. Phys. Chem. Lett.* **9** 756
[4] Trabattoni A *et al* 2015 *Phys. Rev. X* **5** 041053

* E-mail: fernando.martin@uam.es