Valence and Inner-Shell Photoionization Cross-Sections of Free and Adsorbed Molecules Using CCSD and TDDFT Methods

Bruno N. C. Tenório[*], Alexandre B. Rocha, Marco Antonio Chaer Nascimento
Instituto de Química, Universidade Federal do Rio de Janeiro
chaer01@gmail.com

Photoionization cross-sections are very important to understand a large number of phenomena, such as optical refractivity and for interpreting the photoelectron spectra of free and adsorbed species. The main difficulty in determining photoionization cross-sections resides in the calculation of continuum wave functions. The complex dynamic polarizability contains both the absorptive and dispersive information about the system. Thus, photoionization cross sections can be obtained once a representation is found for the complex polarizability. This can be achieved by using a discrete basis set L^2 to represent both the bound and the continuum states of the system[1,2]. This discrete representation of the continuum is used to construct an approximation to the complex dynamic polarizability, $\alpha(z) = \sum_{n \neq 0} \frac{f_{on}}{w_{on}^2 - z^2}$, which is then used in an analytical continuation procedure with Padé approximants[2]. The spectral moments which are the input to our approximation of the complex dynamic polarizability can be obtained with a variety of methods for electronic structure as, for example, coupled cluster damped linear response theory based on the asymmetric Lanczos algorithm[3] at the coupled cluster singles and doubles level (CCSD). Kauffman et. al.[4] provided a set of Gaussian primitives that are able to reproduce some properties of the continuum region. These continuum-like Gaussian basis functions were used throughout our work. In this talk we present results for valence and inner shell photoionization cross sections for several free and adsorbed molecules[5-8]. Dunning's correlation consistent aug-cc-pVTZ basis set plus additional Kauffman[4] type continuum-like Gaussian basis functions placed on the center of mass of the molecule with quantum numbers ranging from 3 to 10 have been employed. The calculations were carried out at the experimental equilibrium geometries (CNPq, FAPERJ).

[1] P. W.Langhoff, Chem. Phys. Lett. 22, 60 (1973).
[2] M.A.C. Nascimento, W.A. Goddard III, *Phys. Rev A* **16**, 1559 (1977); M. A. C. Nascimento, *J. Mol. Struct.* **120**, 227 (1985); E. Hollauer, M. A. C. Nascimento, *Phys. Rev. A* **42**, 6608 (1990).
[3] Cukras et. al. *J. Chem. Phys*. **139**, 094103 (2013).
[4] K. Kauffmann, W. Baumeister, M. Jungen, *J. Phys. B: At. Mol. Opt. Phys.* **22**, 2223 (1989).
[5] B.N.C. Tenório, M.A.C. Nascimento, A.B. Rocha, *J. Chem. Phys*. **148**, 074104 (2018)
[6] B.N.C. Tenório, M.A.C. Nascimento, A.B. Rocha, *J. Chem. Phys*. **150**, 154308 (2019)
[7] B.N.C. Tenório, R.R. Oliveira, M.A.C. Nascimento, A.B. Rocha, *J. Chem. Theory Comput.* **14**, 5324 (2018)
[8] B.N.C. Tenório, M.A.C. Nascimento, A.B. Rocha, *J. Phys. Chem.* **124**, 2591 (2020)